BPI Biodegradable Products Institute

March 23, 2012

Lisa Brines, PhD
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USDA/AMS/NOP, Standards Division
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Dear Dr. Brines,

Thank you for accepting our petition dated 1/19/2012. We acknowledge your reference to Section 2109 of the Organic Foods Production Act of 1990 (OFPA) that requires plastic mulches be removed at the end of the growing or harvest season [7 U.S.C. 6508]. In order to clarify our petition and directly address this requirement in OFPA, we request that the enclosed revised **Biodegradable Mulch Film Made From Bioplastics** petition and justification statement replace the previously submitted plastic mulch petition.

In 1990, when plastic was referenced in OFPA it was not equivalent nor intended to reference biodegradable mulch film. Predominantly plastic mulches, as referenced in OFPA, are made from traditional petroleum-based plastics, such as polyethylene since biodegradable mulch films made from bioplastics were not commercially available at the time.

Polyethylene is a polymer joined by carbon-to-carbon bonds, which are resistant to biological digestion by almost all organisms and their enzymes, because there is no other functional group on the polyethylene chain that would give the enzyme ‘purchase’ so it could do its work. In contrast, the bioplastics being petitioned are polyesters, polymers formed by the reaction of a hydroxyl group and a carboxyl group. The natural world is full of ester linkages. Living cells and organisms have developed enzymes to hydrolyze the ester linkage. Examples of natural esters are fats and oils, where three fatty acid molecules are esterified to glycerol/glycerin; natural waxes, where long-chain alcohols are esterified to a fatty acid; and some natural flavors, such as banana flavor, n-amyl acetate, an ester of n-amyl alcohol and acetic acid.

Biodegradable mulch films made from bioplastics are the subject of this petition. The restriction within OFPA to remove plastic mulch at the end of each growing or harvest season should not be applicable to biodegradable films because these are not the plastics referenced in the law. By definition and intention, a biodegradable mulch film is substantially biodegraded by the end of the growing season or by the beginning of the following growing season, so its removal would be difficult and may be physically impossible.

We believe that this revised petition should provide the National Organic Standards Board, the National Organic Program and the stakeholders in the organic community with the necessary clarification and explanation of biodegradable mulch film made from bioplastics and how these materials are compatible with the principles of organic agriculture and satisfy the criteria for the National List, as well as how these materials meet the requirements of OFPA and the National Organic Program Rules.

Biodegradable Products Institute (BPI) represents the major manufacturers of biodegradable films in the United States. We are available to provide any additional information that is needed to complete your review process and recommendation.

Sincerely,

Steven Mojo

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INTRODUCTION

Plastic films have been used as mulch in vegetable production since the 1950s. Predominantly, these are made from traditional plastics, such as polyethylene. As mulch, plastic films have served many functions, such as weed prevention, moisture retention and to raise soil temperatures, all of which contribute to higher crop quality.

Many organic vegetable farmers rely on plastic mulch for weed control, moisture retention, and soil warmth. At the end of the growing season it must be pulled and thrown out, which adds trash to landfills, takes a lot of time, and delays cover cropping. Unfortunately, plastic mulch is often made from a non-renewable resource and has disposal issues. “There is estimated to be 100-120 lb/acre of un-recyclable, petroleum-based waste that farmers must pay to landfill at season’s end. Soil and crop residue on the recovered plastic have made recycling impractical to date. (Grantham, 2011)” In 1999, more than 30 million acres of agricultural land worldwide were covered with plastic mulch, and those numbers have been increasing significantly since then.

In today’s world, characterized by new “green” technologies and materials that may help to reduce or control waste generation and disposal, there is substantial drive for commercial manufacturers to develop biodegradable films to be used as mulch. These biodegradable films are produced from bioplastics and meet standards for aerobic biodegradation in soil. These bioplastics are comprised of structural units which may be easily broken down into carbon substrates by soil microorganisms. Under aerobic conditions, these microorganisms are able to utilize the carbon substrates as a food source. This metabolism of the carbon substrates ultimately results in two simple compounds – carbon dioxide and water.

These biodegradable mulches provide numerous advantages over the traditional polyethylene plastic films - the most notable being the elimination of the need to remove them from the fields at the end of the growing season. Since the soil microorganisms completely assimilate the polymers used to make these films, these mulches can be simply tilled into the soil to naturally degrade, a process that takes less than 2 years. This saves considerable costs in labor, transport and landfill disposal.

ITEM A

When the OFPA was enacted on November 28, 1990, the universal plastic mulch in the United States was polyethylene plastic. Polyethylene plastic mulch, although recognized as a beneficial tool on organic farms, does not break down and enrich the soil. It is for this reason that OFPA contained Sec. 2109(c)(2) [7 U.S.C. 6509]: “(c) Crop Management. – For a farm to be certified under this title, producers on such farm shall not – (2) use plastic mulches, unless such mulches are removed at the end of each growing or harvest season.”

But removal and disposal of polyethylene plastic has negative environmental, social and economic impacts. The problems of polyethylene plastic removal and disposal stimulated research and development on biodegradable mulch films with equivalent efficacy to polyethylene plastic mulch. The culmination of a half-century of research and development is the biodegradable films that are the subject of this petition.

Polyethylene is a polymer joined by carbon-to-carbon bonds, which are resistant to biological digestion by almost all organisms and their enzymes, because there is no other functional group on the polyethylene chain that would give the enzyme ‘purchase’ so it could do its work. In contrast, the bioplastics being petitioned are polyesters, polymers formed by the reaction of a hydroxyl group and a carboxyl group. The natural world is full of ester linkages. Living cells and organisms have developed enzymes to hydrolyze the ester linkage. Examples of natural esters are fats and oils, where three fatty acid molecules are esterified to glycerol/glycerin; natural waxes, where long-chain alcohols are esterified to a fatty acid; and some natural flavors, such as banana flavor, n-amyl acetate, an ester of n-amyl alcohol and acetic acid

The National Organic Program (NOP) Rule at §205.2 defines “Mulch” as “any nonsynthetic material, such as wood chips, leaves, or straw, or any synthetic material included on the National List for such use, such as newspaper or plastic that serves to suppress weed growth, moderate soil temperature, or conserve soil moisture.”

§205.206 permits, as part of the “Crop pest, weed, and disease management practice standard,” that “(c) Weed problems may be controlled through:

(1) Mulching with fully biodegradable materials;

(2) Mowing;

(3) Livestock grazing;

(4) Hand weeding and mechanical cultivation;

(5) Flame, heat, or electrical means; or

(6) Plastic or other synthetic mulches: Provided, That, they are removed from the field at the end of the growing or harvest season.”

§205.203 of the Rule establishes, as part of the “Soil fertility and crop nutrient management practice standard,” that “(d) A producer may manage crop nutrients and soil fertility to maintain or improve soil organic matter content in a manner that does not contribute to contamination of crops, soil, or water by plant nutrients, pathogenic organisms, heavy metals, or residues of prohibited substances by applying: (5) A plant or animal material that has been chemically altered by a manufacturing process: Provided, That, the material is included on the National List of synthetic substances allowed for use in organic crop production established in Sec. 205.601.”

The National List at §205.601(b)(2) includes, among the synthetic substances that may be used in organic crop production (provided that use of such substances do not contribute to contamination of crops, soil, or water), ”Mulches” and lists two specifically:

(i) Newspaper or other recycled paper, without glossy or colored inks.

(ii) Plastic mulch and covers (petroleum-based other than polyvinyl chloride (PVC)).

This petition seeks inclusion of **Biodegradable Mulch Film Made From Bioplastics**[1] on the National List at §205.601(b) as a synthetic substance allowed for use in organic crop production. Biodegradable mulch film is defined as mulching materials that:

1) *meet the requirements of ASTM Standard D6400 or D6868 specifications, or of other international standard specifications with essentially identical criteria, i.e. EN 13432, EN 14995, ISO 17088; and*
2) *show at least 90% biodegradation absolute or relative to microcrystalline cellulose*[2] *in less than two years, in soil, tested according to ISO 17556 or ASTM 5988.*

The current Rule has an internal contradiction with respect to "biodegradable mulch film made from bioplastics." §205.206(c)(1) permits "mulching with fully biodegradable materials" but §205.206(c)(6) requires that "plastic or other synthetic mulches . . . are removed from the field at the end of the growing or harvest season." By definition and intention, a biodegradable mulch film made from bioplastics is substantially biodegraded by the end of the growing season or by the beginning of the following growing season, so its removal would be difficult and may be physically impossible. Moreover, requiring removal would obviate the major environmental and economic benefit of biodegradable mulch film made from bioplastics, said benefit being that biodegradable mulch film made from bioplastics eliminates the disposal issue currently faced by producers using non-biodegradable plastic (polyethylene) mulch.

The structure of the current Rule needs to be revised to accommodate mulching with biodegradable mulch film. We recommend that §205.206(c)(6) be amended by addition of the term "non-biodegradable" to read "**Non-biodegradable** plastic or other synthetic mulches… are removed from the field at the end of the growing or harvest season."

The Rule currently authorizes mulching with fully biodegradable materials at §205.206(c)(1). A critical aspect in interpreting §205.206(c)(1) and in applying it to materials is having an enforceable working definition of the term "fully biodegradable" when referred to bioplastics ending up in soil, as in the case of biodegradable mulch film made from bioplastics which is designed not to be removed after harvest season.

"Full biodegradation" is addressed by several standards dealing with compostability of these products. ASTM (formerly known as the American Society for Testing and Materials) has developed relevant standards for biodegradability of bioplastic in soil, ASTM Standard D5988, and in compost, ASTM Standard D6400 and D6868 specifications. These standards or other international standard specifications with identical or more stringent criteria for bioplastics, i.e. ISO 17556, EN 13432, EN 14995, ISO 17088, or "OK Soil" by Vinçotte, should be referenced as

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[1] According to European Bioplastics' definition, bioplastics are biobased, biodegradable, or both. The ASTM definition of "biobased material" is "organic material in which carbon is derived from a renewable resource via biological processes. Biobased materials include all plant and animal mass derived from CO_2 recently fixed via photosynthesis, per definition of a renewable resource." The ASTM definition of "biodegradable plastic" is "a degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi, and algae."

[2] Relative biodegradation is compared with the biodegradation obtained by cellulose microcrystalline tested in parallel and for the same duration.

the definition of “fully biodegradable”. Copies of the abstracts for these standards are available in Appendix A.

The equivalent European standards EN 13432 *(Packaging - Requirements for Packaging Recoverable through Composting and Biodegradation -Test Scheme and Evaluation Criteria for the Final Acceptance of Packaging)* and EN 14995 *(Plastics - Evaluation of Compostability – Test Scheme and Specifications)*, have been published in the Official Gazette of the European Union, and have consequently been adopted by every European country. These standards are used by European organic certifiers. Copies of the abstracts for these three standards also are included in Appendix A.

ISO Standard 17088 *(Specifications for Compostable Plastics)*, was recently adopted as a reference for compostable plastic and items thereof by BNQ CANADA.

According to said standards, full biodegradation is proved when the percentage of biodegradation is at least 90% in total or 90% of the maximum degradation of a suitable reference substance (Microcrystalline cellulose) after a plateau has been reached for both test material and reference substance, within a six month time span.

Biodegradation is based on conversion of the carbon of the test material into carbon dioxide and biomass. This is the reason why the standards request 90% rather than 100%, because part of the carbon in the material is not immediately turned to CO_2 and water, (mineralization) but stored by microorganisms.

Biodegradation is tested in conditions that simulate the composting process.

Since the final compost will end up in soil, all the above mentioned standards address the ecotoxicity characterization of the final compost by means of OECD-based ecotoxicity test (germination and growing tests) and by fixing strict limits for some chemical elements of concern, such as heavy metals.

The main point in doing the ecotoxicity tests is to safeguard the soil in which the final compost will end up, when applied as a natural source of fertilization and a natural soil improver.

Generally speaking, the composting environment is the most aggressive in terms of biodegradation especially because of the high temperature that accelerates metabolism and the chemical reactions.

A material that is biodegradable under composting conditions could turn out to be less biodegradable when exposed to lower temperature. On the other hand, we can state materials that are not biodegradable under composting conditions are very unlikely to be biodegradable at lower temperature. Therefore the compliance to the above mentioned standards can be considered as a prerequisite, a condition that is necessary even if not sufficient.

As a matter of fact, biodegradation at low temperature must be demonstrated.

Specifications for biodegradable mulch (NF U 52 001) has been developed by AFNOR, the French standardization body.

Additionally the Certification Institute Vinçotte (Brussels, Belgium) has elaborated a certification scheme to respond to the market need for a workable definition of biodegradation of plastic in soil. Said certification scheme is called "Program OK10-Bio-products: biodegradation in soil" Copies of this certification scheme are available in Appendix A. Materials certified to the above mentioned Vinçotte scheme receive the "OK BIODEGRADABLE SOIL" conformity mark.

The following chart identifies international standards for biodegradable plastic mulch.

Table 1. a synoptic view of standards.

Location	**Standard**	**Scope**	**Certification**
Europe	EN 13432	Organic recycling of packaging	AIB-Vinçotte (Belgium) DIN-Certco (Germany) CIC (Italy) Jatelaito-syhdistys (Finland)
Europe	EN 14995	Compostability of bioplastics	AIB-Vinçotte (Belgium) DIN-Certco (Germany)
International	ISO 17088	Compostability of bioplastics	Canada BNQ 9011-911 DINCertco (Germany)
North America	ASTM D6400	Compostability of bioplastics	BPI/USCC
North America	ASTM D6868	Compostability of products	BPI/USCC
Italy	UNI 11183	Biodegradation of bioplastics at room temperature	I.I.P. (Italy)
France	NF U 52-001	Biodegradable mulch	SERPBIO (France)
Belgium	OK Biodegradable Soil	Aerobic biodegradation in soil	AIB-Vinçotte (Belgium)
International	ISO 17556	Aerobic biodegradation in soil	N/A
North America	ASTM D5988	Aerobic biodegradation in soil	BPI/USCC

Based on the above, “fully biodegradable mulch films” are those that:

1) *are made with material fulfilling ASTM D6400 or EN 13432, or EN 14995 or ISO 17088; and*
2) *show at least 90% biodegradation (absolute or relative to microcrystalline cellulose) within two years time, proven by ISO 17556 or ASTM D5988.*

The first requisite is aimed at proving inherent biodegradability of the bioplastic material and the absence of ecotoxic effects after the biodegradation has been accomplished; given that under ASTM or EN “compostability” standards biodegradation is proved in simulated composting conditions (i.e. at 58°C and in a very active biological environment), this can be regarded as an “accelerated” biodegradation test.

The second requisite is aimed at confirming that biodegradation will ultimately take place in milder biological conditions such as those found in soil (at lower temperature).

The materials described in this petition are examples of biodegradable mulch films that comply with both requisites. Current petition seeks for listing at §205.601 the “fully biodegradable materials” fulfilling the above mentioned two requisites.

Item B

1. The chemical or material common name of Biodegradable Mulch Film Made From Bioplastics

Biodegradable Mulch Film Made From Bioplastics is defined as mulching material that meets both of the following requirements.

1. Compliance with the specifications of ASTM Standards D6400 or D6868 or other international standard specifications with identical criteria, i.e. EN 13432, EN 14995, ISO 17088. This compliance will conclusively prove that these materials will biodegrade and not negatively impact the ability of the soil to grow plants, and also that these products will not introduce high levels of regulated metals
2. Demonstration that they will fully biodegrade (90%) at ambient temperatures in two years, using ASTM Standard D5988 or ISO 17555 (both soil biodegradation tests) or meeting the requirements of AIB Vinçotte’s “OK Soil” certification

Four forms of bioplastics in mulch films currently available and being used in organic production systems in Canada and Europe satisfy this definition.

BioTelo is an example of biodegradable mulch film made from Mater-Bi®, a corn starch based bioplastic material. Garden Bio-Film, known also as BioBag AgroFilm, also is made from the material, Mater-Bi®. The biodegradable bioplastic, Mater-Bi®, is produced by Novamont, an Italian company that produces biodegradable and compostable bioplastic materials. Mater-Bi® is a wide family of fully biodegradable bioplastics (Mater-Bi® “grades”), sold in pellet form to the industry of bioplastic converters, for the production of several articles such as compostable shopping bags, organic waste collection bags, mulch films, cutlery items etc.

Mater-Bi®'s ingredients consist of starches derived from plants, mainly corn starch, and fully biodegradable aliphatic-aromatic polymers from both renewable raw materials (mainly vegetable oils) and fossil raw materials. The specific Mater-Bi® grades devoted to mulch film meet ASTM D6400 specifications. Additionally, they "break down into carbon dioxide and water, with no mulch residues in the soil” (Cornell University 2006, Biodegradable Mulch Product Testing).

NatureWorks’ PLA INGEO™ is one of a broad family of over 15 plant based Ingeo™ biopolymer grades produced in NatureWorks' world scale, 140,000 ton/year capacity facility in Blair, Nebraska. PLA indicates that the biopolymer contains polylactic acid. Ingeo™ grades are certified compostable by BPI according to the ASTM D6400 standard. Other companies manufacturing products based on these Ingeo™ grades must independently confirm that their products meet this standard if they wish to so claim. In addition to offering composting options where appropriate for the product and local infrastructure, Ingeo™ grades offer the option of feedstock recovery via hydrolysis back to the lactic acid starting monomer.

Ecoflex® F Blend C1200 is a biodegradable aliphatic-aromatic copolyester produced by BASF from the monomers 1,4-butanediol, adipic acid and terephthalic acid. BASF also produces Ecovio® F Film and Ecovio® F Blend products that are basically mixtures of Ecoflex® F Blend and polylactic acid (PLA) produced with various contents of renewable resources.

Mirel™ is a bioplastic made by Metabolix from polymers known as polyhydroxyalkanoates (PHA). Polyhydroxyalkanoates are linear polyesters produced in nature by bacterial fermentation of sugar and lipids. These polymers contain repeating units of 3-hydroxybutyric acid and 3-hydroxyvaleric acid and are produced within the cells of microorganisms[3]. Metabolix formed a joint venture with Archer Daniels Midland, called Telles, to market its bioplastic, which it sells under the brand name Mirel™.

Each of these biodegradable bioplastic mulch film materials may contain carbon black to color the film black so it absorbs heat from sunlight or titanium dioxide to create a white mulch film, which can reduce surface soil temperatures slightly, by about a half a degree at a 2-inch depth relative to bare soil, because it reflects most incoming radiation. White mulch film is useful when lower soil temperatures are desired for summer production.

Note that there is another mulching material that might qualify as “biodegradable plastic mulch.” A material described as “paper mulch” comprised of kraft paper coated with cured vegetable oil-based resins. Vegetable oil-based resin may qualify the material as “plastic”[4]. This material, however, is not included within the scope of this petition.

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[3] Anderson AJ, Dawes EA. Microbiol Rev. 1990 Dec;54(4):450-72. Occurrence, metabolism, metabolic role, and industrial uses of bacterial polyhydroxyalkanoates.

[4] Plastic (ASTM definition ASTM D883): a material that contains as an essential ingredient one or more organic polymeric substances of large molecular weight, is solid in its finished state, and, at some stage in its manufacture or processing into finished articles, can be shaped by flow.

Materials that are subjected to photo-degradation/thermo-degradation (and frequently commercially named as “oxo-biodegradable”) are not included within the scope of this petition. Reference to these materials can be found in the attached literature dealing with mulch film performance. They have been used in studies in recent years where their performance was compared to the performance of biodegradable mulch materials. Oxo-biodegradable materials did not fulfill the two criteria proposed to address the concept of “fully biodegradable plastics”.

2. Manufacturer’s name, address and telephone number and other contact information.

(a) Producers of Biodegradable Mulch Film Made from Bioplastics

Some examples of biodegradable mulch films are provided hereafter. The list is not exhaustive and other brands may be found in the market.

Garden Bio-Film and BioBag Agro Film are produced by BIOgroupUSA, Inc. P.O. Box 369, Palm Harbor, FL 34682-0369; Tel: (727) 789-1646, Fax: (727) 489-6865; http://www.biobagusa.com

BioTelo is produced by PROTEMA s.r.l., located in Piazzale Biancamano, 2 – 20121 Milano, Italy; Tel: +39 02 2563336, Fax: + 39 02 2564458; http://www.protema.com

Mirel is produced by the Metabolix/ADM joint venture, Telles, which is located at 650 Suffolk St., Suite 100, Lowell, MA 01854; Tel: (978) 513-1851; http://www.mirelplastics.com

(b) Manufacturers of Biodegradable Bioplastics for various uses, including mulch film production

BASF SE is located in Ludwigshafen, Germany. Their address is D-67056 Ludwigshafen, Germany; tel. +49-621-60-0; http://www.basf.com.

BASF Corporation is located in Florham Park, NJ and markets Ecoflex and Ecovio products throughout North America. Offices are located at 100 Campus Drive, Florham Park, NJ (513) 314-6359; http://www.Bioplastics.basf.com.

NatureWorks L.L.C. is located at 15305 Minnetonka Blvd., Minnetonka, MN, 55345; tel. (952) 562-3400; http://www.natureworksllc.com.

Novamont S.p.a.is located in Via G. Fauser 8, 28100 Novara, Italy +39 0321 699 611;

Novamont North America sells Mater-Bi® in US and is located at 107 Mill Plain Road Suite 300, Danbury, CT 06811; tel. (203) 438 5904; http://www.novamont.com.

Metabolix is located at 21 Erie St., Cambridge, MA 02139; tel. (617) 583-1700; http://www.metabolix.com.

3. The intended or current use of Biodegradable Mulch Film Made from Bioplastics.

Biodegradable mulch film is used in accordance with §205.206 to control weed problems as an occlusive mulch and to improve crop yields by minimizing competitive weed pressure, maintaining soil moisture levels, and modulating soil temperature.

4. Biodegradable Mulch Film Made From Bioplastics is used as a biodegradable mulch allowable at §205.206(c)(1) to control weed problems in diverse horticultural crops such as squash, tomato, watermelon, grapes vines, peppers, and eggplants.

Biodegradable mulch film is applied to the soil from a 4-foot or 5-foot wide roll of about 0.6-mil film (10-30 micron). The edges of the film are covered with soil to prevent displacement by wind, etc., over the growing season. At the end of the growing season that mulch can be turned into the soil or left exposed to continue the biodegradation process.

5. The source of the substance and a detailed description of its manufacturing or processing procedures from the basic component(s) to the final product.

Bioplastics are made with polymers. Polymers are made up of repeating units called "monomers." The synthetic polymers in these biodegradable bioplastics are “polyesters.” An ester is a compound formed from an organic acid, which has a carboxyl group, and an alcohol, which has a hydroxyl group. The “monomer” in biodegradable bioplastics can be a molecule that contains both a carboxyl group and a hydroxyl group, such as lactic acid, or the “monomers” can be molecules with either two carboxyl groups or two hydroxyl groups that are linked ”end-to-end.”

Polymers are made into bioplastics using “processing aids” that act as plasticizers and lubricants. Pigments are added to mulch film to block light transmission and thus prevent weed growth.

(a) Monomers

Table 2.

Monomer	CAS No.	Source	Comment
Lactic acid (L-, D-, DL-)	50-21-5	Fermentation from glucose by microorganisms	Normal physiological metabolite
3-hydroxy-butyric acid	300-85-6	Created within the cell of the fermenting microorganism and converted directly into a storage carbohydrate with plastic properties	Normal physiological metabolites but these hydroxyl acids are not isolated as such
3-hydroxy-valeric acid	10237-77-1		
Adipic acid	124-04-9	Oxidation of cyclohexane	Found in beet juice

Table 2. (continued)

Monomer	CAS No.	Source	Comment
Azelaic acid	123-99-9	Oxidation of ricinoleic acid	Occurs in rancid oleic acid
Sebacic acid	111-20-6	Heating castor oil with sodium hydroxide	Sebacic acid is a normal urinary acid
Terephthalic acid	100-21-0	Oxidation of *p*-methylacetophenone	
1,4-Butanediol	110-63-4	Acetylene and formaldehyde react to form 1,4-butynediol, which is then hydrogenated	
1,3-propylene glycol	504-63-2	Hydration of acrolein or fermentation of corn syrup	
1,6-hexanediol	629-11-8	Hydrogenation of adipic acid	

Lactic acid, which is known chemically as 2-hydroxypropionic acid, contains both a hydroxyl group and a carboxyl group in the same molecule, thus enabling molecules of lactic acid to react with each other, forming a polymer called polylactic acid. The process for producing biodegradable plastics containing polylactic acid is described in U.S. Patents Nos. 6,787,613 and 7,067,596 (Appendix B).

The repeating units in polyhydroxyalkanoic acid are 3-hydroxybutyric acid and 3-hydroxyvaleric acid, each of which contains both a hydroxyl group and a carboxyl group in the same molecule. The fermenting microorganism can produce these monomers from sugars and lipids and then link the molecules to one another, creating the polymer called polyhydroxylalkanoate (PHA). The fermenting microorganism converts sugar and lipid directly to PHA, so these hydroxyacids are not isolated. U.S. Patent Application Publication No. 20080275208 (Appendix B) describes how polyhydroxyalkanoates (PHA) are formed.

The aliphatic-aromatic polyesters used to make biodegradable bioplastics are formed by reacting “diacids,” molecules containing two carboxyl groups, and “diols,” molecules containing two hydroxyl groups. Typical diacids are adipic acid, azelaic acid, sebacic acid, and terephthalic acid. Typical diols are 1,3-propylene glycol, 1,4-butanediol, and 1,6-hexanediol. Each of these molecules, called generically “monomers,” is 100% biodegradable. The ester linkage is hydrolyzed by soil bacteria.

Some biodegradable bioplastics contain a nonsynthetic polymer, native non-chemically modified corn starch. Corn starch and other starches are polymers of glucose that both higher organisms and microorganisms can hydrolyze and then use the glucose for energy.

Mater-Bi® biodegradable bioplastic contains corn starch coextruded with synthetic aliphatic-aromatic polyesters.

(b) Processing Aids

U.S. Patent No. 6,096,809 (Appendix B) describes how polymers are blended together and formed into film and discloses the plasticizer used. U.S. Patent No. 6,7787,613 (Appendix B) discloses the aliphatic acid amides added to improve film-forming characteristics.

Processing Aid	CAS No.	Source	Comment
Glycerol (glycerin)	56-81-5	Obtained from oils and fats	Glycerol, food grade, is a GRAS substance
Stearamide	124-26-5	Stearic acid is reacted with ammonia	Stearic acid is a normal food fatty acid
Erucamide	112-84-5	Erucic acid is reacted with ammonia	Erucic acid is a major fatty acid in rapeseed oil and mustard seed oil

The preferred plasticizer in aliphatic-aromatic polyester plastics is glycerol (glycerin), a substance on the National List at §205.605(b). Compounds formed by reacting natural fatty acids with ammonia, called “aliphatic acid amides,” can be added to improve the film-forming characteristics of the material.

(c) Pigments

Carbon black, CAS No. 1333-86-4, is added to black biodegradable mulch films at a level of about 2% to 4%. Carbon black is a generic term for a particulate form of elemental carbon manufactured by the vapor-phase pyrolysis and partial combustion of hydrocarbons. Over 95% of all carbon black produced today is furnace black.

Titanium dioxide, CAS No. 13463-67-7, is used to create white plastic mulch. Titanium dioxide is obtained from a variety of ores that contain ilmenite, rutile, anatase and leucoxene, which are mined from deposits located throughout the world. Most titanium dioxide pigment is produced from titanium mineral concentrates by the chloride or sulfate process, either as the rutile or the anatase form. The primary particles are typically between 0.2 and 0.3 μm in diameter, although larger aggregates and agglomerates are formed. Ultrafine grades of titanium dioxide have a primary particle size of 10–50 nm and are used predominantly as ultraviolet blockers in sunscreens and plastics, and in catalysts.

6. A summary of any available previous reviews by State or private certification programs or other organizations of the petitioned substance.

(a) Certifications of the basic materials

Mater-Bi® materials, manufactured by Novamont S.p.A. have multiple composting and biodegradability certificates. They are certified ‘biodegradable and compostable’ under the EN 13432 and EN 14995 standards for Europe and under the ASTM D6400 standard for the United States, and some materials have received similar compostability certifications in other countries (according to AS 4736 in Australia, according to GreenPLA system in Japan).

Additionally, the specific Mater-Bi® materials sold for the mulch film production are certified “OK biodegradable soil” under the Vinçotte certification program OK10, described under ITEM A.

Examples of certifying bodies operating in the biodegradable and compostable plastics sector are BPI (US), CIC-Certiquality (Italy), DIN Certco (Germany) and Vinçotte (Belgium).

NatureWorks’ Ingeo™ carries the "OK biobased" certification from Vinçotte. This certification is based on the biobased content of Ingeo which can be determined through radiocarbon dating according to ASTM D6866-5 (Standard Test Method for Determining the Biobased Content of Natural range Materials Using Radiocarbon and Isotope Ration mass Spectrometry Analysis). It also maintains certification as compostable by the Biodegradable Products Institute as well as inclusion in Japan’s GreenPLA Category A (Biodegradable Plastics) list.

BASF’s Ecoflex® biodegradable bioplastic is certified by the Biodegradable Products Institute in North American via ASTM D6400, and has biodegradable certifications with the European Standard EN 13432 on compostability as well as the Japanese standard GreenPla.

Telles’ Mirel™ is certified compostable by the Biodegradable Products Institute and carries the “OK compost” certification from Vinçotte (EN 13432) as well as “OK biodegradable SOIL” certification.

(b) Certifications of the mulch film products

A European plastic converter, GroupBarbier, known to use Mater-Bi and other biodegradable bioplastic materials, had the biodegradable mulch films, sold under the trade names BIONOV® and BIOFILM®, approved for organic use by EcoCert France.

(c) Regulatory overview outside of the U.S.

In 2011, the Canada Organic Standard Permitted Substance List was amended to allow the use of ***fully biodegradable films*** without removal if they do not contain substances prohibited by par. 1.3.1 of CAN/CGSB-32.310, Organic Production Systems – General Principles and Management Standards such as, all material and products produced from genetic engineering, sewage sludge, and intentionally manufactured nano-technology products.

7. Information regarding EPA, FDA, and State regulatory authority registrations, including registration numbers.

Carbon black and titanium dioxide have been reviewed by EPA as an inert ingredient. The EPA reports are available in Appendix C.

The aliphatic-aromatic polyester used in Mater-Bi® is listed on the Toxic Substances Control Act (TSCA) Inventory. EPA did not place any restriction or limitation on the polymer.

NatureWorks' Ingeo™ PLA has been reviewed with regard to the manufacture of food contact articles by FDA and assigned the Food Contact Notification Numbers FCN 000175 and FCN 000475.

Primary components of BASF's Ecoflex® and Ecovio® have been reviewed by FDA's Environmental Review Team with regard to use as films, coatings and food contact articles. Reference Food Contact Notification Numbers FCN 000907, FCN 000372, FCN 000780, FCN 000175 and FCN 000475.

The polyhydroxyalkanoate polymers produced by Metabolix is listed on the Toxic Substances Control Act (TSCA) inventory with no restrictions or limitations on the polymer. Metabolix has also been reviewed with regard to the manufacture of food contact articles by FDA and assigned the Food Contact Notification Number FCN 000943.

8a. The Chemical Abstract Service (CAS) number or other product numbers of the substance.

Biodegradable mulch films made from bioplastics do not have assigned CAS numbers. Item B.5. lists the CAS numbers of the monomers used to produce biodegradable bioplastics.

The biodegradable bioplastics used to produce these mulch films have the following CAS numbers.

Ingeo™ PLA: CAS No. 9051-89-2

Ecoflex® F Blend C1200: CAS No. 60961-73-1

Mater-Bi® NF 803P: CAS No. 944131-90-2

Mirel™ 4000 Series is comprised of the following two co-polymers -

PHB - Butanoic acid, 3-hydroxy-, (3R)-, homopolymer: CAS No. 29435-48-1

PHB4HB - Butanoic acid, 3-hydroxy-, (3R)-, polymer with 4-hydroxybutanoic Acid: CAS No. 125495-90-1

8b. Labels for Biodegradable Mulch Film Made From Bioplastics.

See Appendix D.

9. The substance's physical properties and chemical mode of action.

Mulch film is used as an intact occlusive film to control weeds, reducing the competition for nutrients intended for the desired horticultural crop.

Biodegradable bioplastic mulches are applied as films that slowly degrade to carbon dioxide and water. As they are exposed to the soil, soil microbial enzymes that hydrolyze esters and starch break the polymers down to simpler molecules. These simpler molecules in turn are sources of energy for microorganisms.

Film used for mulching frequently contains pigment for color.

Black mulch film contains carbon black. The color and opacity of black mulch film cause it to absorb light, converting sunlight to heat which warms the soil. Carbon black also reduces the rate of UV-accelerated photodegradation of film.

Titanium dioxide is added to white mulch films. Titanium dioxide blocks visible and ultraviolet light transmission.

(a) Chemical interactions with other substances, especially substances used in organic production

The monomers and other components of clear film mulch are totally biodegradable.

Carbon black adsorbs toxic molecules in the soil, increasing crop growth in contaminated soils.[5]

Titanium dioxide is found in nature as the minerals rutile (tetragonal), anatase or octahedrite (tetragonal), brookite (orthorhombic), ilmenite (FeTiO3), and perovskite (CaTiO3). It is inert and unreactive.

(b) Toxicity and environmental persistence

The polymers used to make these bioplastic mulch films are 100% biodegradable to carbon dioxide and water. Therefore, these polymers do not persist in the soils.

The only non-biodegradable components are the pigments used to provide color and reduce light transmission. Carbon black contributes the black color and opacity to mulching film. Carbon black, also known as "lampblack," is a material produced by the incomplete combustion of heavy petroleum products such as tar. Carbon black is a form of amorphous carbon that has a high surface-area-to-volume ratio. Carbon black particles are familiar to most people because of their use in photocopier and laser printer toner.

No significant environmental hazards are associated with carbon black released to the environment[6]. In 2005, EPA reviewed carbon black as an inert and concluded that it can be

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[5] Skinner, J.J., and Beattie, J.H. 1916. A study of the action of carbon black and similar absorbing materials in soils. Soil Science, 2(1) 93-101 (See Appendix 7)

[6] http://www.idph.state.il.us/pdf/JuneFlood_Carbon.pdf accessed 26 October 2011.

reclassified from List 3 to 4B. EPA concluded that "it (carbon black) is not soluble in water or any other commercial solvents. Carbon black is not subject to degradation per se because it is not expected to photolyze, hydrolyze, or (be) subject to metabolic degradation. . . It is an inert material and does not harm water or the environment. It is adsorb(ed) to the soil and does not harm soil or the crops grown on such soils."[7]

Carbon black persists in the soil for a long time. It is part of the "black carbon" fraction of the soil. Over time it gradually oxidizes.[8]

Titanium dioxide is an inert mineral found in nature. It is exempt from the requirement of a tolerance when used as a pigment/coloring agent in plastic bags used to wrap growing bananas or as a colorant on seed for planting as an inert ingredient in pesticide formulations.

Heavy metals are a concern with certain sources of compost. All of these biodegradable plastics contain less than the maximum allowance in the U.S. (ASTM), Canadian, and European heavy metal standards. The European standards for heavy metals are substantially lower than the US or Canadian standards, as the following chart documents.

	Limits for U.S. (ppm)	**Limits for Canada (ppm)**	**EN 13432 - Annex A (ppm)**
Arsenic	21.5	19	5
Cadmium	19.5	5	0.5
Copper	750	189	50
Lead	150	125	50
Mercury	8.5	1	0.5
Nickel	210	45	25
Selenium	50	4	0.75
Zinc	1400	463	150
Cobalt	NA	38	-
Chromium	NA	265	50
Molybdenum	NA	5	1
Fluorine	-	-	100

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[7] http://www.epa.gov/opprd001/inerts/carbonblack.pdf accessed 26 October 2011.

[8] Cheng , C.-H., Lehmann, J. and Mark H. Engelhard, M.H. 2008. Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence. Geochimica et Cosmochimica Acta 72: 1598–1610. (See Appendix 7)

(c) Environmental impacts from the use and manufacture.

The polymers used to make bioplastic mulch films are fully biodegradable. Their use actually reduces the environmental impact of plastic mulch by displacing black polyethylene sheeting which must be removed from the field at the end of the growing season. It is very difficult to recycle non-biodegradable used polyethylene mulch.

The manufacture of these biodegradable bioplastics occurs in modern factories with state-of-the-art controls and systems to avoid environmental contamination.

The manufacture of Mater-Bi® grades takes place under an integrated management systems certified to ISO9001 (quality management), ISO14001 (environmental management) and OHSAS 18001 (health and safety of workers management).

For some of the polymers (e.g., polylactic acid), the waste can be converted back into the base monomer (lactic acid).

Ingeo™ grades are certified by the Belgian AIB Vinçotte Certification body as 100% biobased, as defined by the ASTM D6866 standard. All Ingeo™ resin grades offer the same eco-profile, conducted according to the Plastics Europe methodology, and are 3rd party reviewed. When compared to amorphous PET using this Plastics Europe methodology, for example, the production of Ingeo™ emits 59% less CO_2 and requires 47% less non renewable energy.

The pigments used to color the film– carbon black and titanium dioxide – are produced as very fine particulates. Modern factories pay great attention to dust control to protect the lungs of workers. Once these pigments are made into plastic, any adverse environmental and health effects are eliminated.

Carbon black was studied almost 100 years ago and found to be a useful soil additive in several different situations.[9]

Titanium dioxide is found in nature.

(d) Effects on human health.

Compared to conventional polyethylene black plastic mulch, the biodegradable mulch film does not need to be removed from the field at the end of the season, thus sparing workers from being exposed to the dust, dirt, and mold that contaminates plastic left outdoors for six to ten months.

Carbon black was re-reviewed in 2005 by EPA, since it is an inert ingredient of some “pesticides.” EPA reclassified carbon black from list 3 to list 4B because of its low risk status. Historically, before 1970, and in undeveloped countries, workers producing or handling

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[9] Skinner, J.J., and Beattie, J.H. 1916. A study of the action of carbon black and similar absorbing materials in soils. Soil Science, 2(1) 93-101 (See Appendix 7)

carbon black were exposed to extremely high levels of airborne carbon black. Exposure studies in this industry in the USA and Western Europe after the late 1970s found personal geometric mean exposures to inhalable dust to be less than 5 mg/m3. By the mid- to late 1990s the geometric mean levels of inhalable dust were below 2 mg/m3. The geometric mean levels of respirable dust were below 0.5 mg/m3. No data were available that would allow the characterization or quantification of exposure to ultrafine primary particles. Exposure in the user industries is difficult to assess because of the lack of data and concomitant exposure to many other particles but exposure levels are assumed to be lower, with the possible exception of workers who handle carbon black in these industries. Exposure to carbon black does not occur during the use of products in which carbon black is bound to other materials, such as rubber, printing ink or paint, or plastic.

Two of the three studies of carbon black production workers observed excess risk for lung cancer and other studies provided mixed evidence for an increased risk for lung and other cancers. The few studies that assessed exposure–response for lung cancer, including the two that observed excess risks compared with the general population, provided weak or inconclusive evidence of a dose–response. Overall, these results led the IARC Working Group to conclude that there was *inadequate evidence* from epidemiological studies to assess whether carbon black causes cancer in humans. There is *inadequate evidence* in humans for the carcinogenicity of carbon black. IARC classified carbon black as "*possibly carcinogenic to humans (Group 2B)*".

Titanium dioxide is a mild pulmonary irritant and is classified as a nuisance dust, without 'innate' toxicity, but with adverse respiratory effects during its manufacture and handling. Persons at risk are those with impaired pulmonary function, especially those with obstructive airway disease. The breathing of titanium dioxide might cause exacerbation of symptoms due to its irritant properties.

Titanium dioxide has a carcinogen rating of "3," since it is not classifiable as to its carcinogenicity to humans. This category is used most commonly for agents, mixtures and exposure circumstances for which the evidence of carcinogenicity is inadequate in humans and inadequate or limited in experimental animals. Exceptionally, agents (mixtures) for which the evidence of carcinogenicity is inadequate in humans but sufficient in experimental animals may be placed in this category when there is strong evidence that the mechanism of carcinogenicity in experimental animals does not operate in humans. IARC reviewed titanium dioxide and concluded that there is *inadequate evidence* in humans for the carcinogenicity of titanium dioxide. They classified titanium dioxide as *possibly carcinogenic to humans (Group 2B).*

Titanium dioxide is generally thought to be unabsorbed from the intestinal tract, although a single clinical study of oral ingestion of fine titanium dioxide showed particle size-dependent absorption by the gastrointestinal tract and large inter-individual variations in blood levels of titanium dioxide. Titanium dioxide is allowed by FDA as a color additive that may be safely used for coloring foods generally, subject to the following restrictions: (1) The quantity of titanium dioxide does not exceed 1 percent by weight of the food. (2) It may not be used to color foods for which standards of identity have been promulgated under section 401 of the act unless added color is authorized by such standards.

Topically, titanium dioxide is devoid of toxicity. It is used as a UV-blocker in suntan lotions. Studies on the application of sunscreens containing ultrafine titanium dioxide to the healthy skin of human volunteers revealed that titanium dioxide particles only penetrate into the outermost layers of the stratum corneum, suggesting that healthy skin is an effective barrier to titanium dioxide.

(e) Effects on soil organisms and crops.

Mulch film increases soil temperature, helps to retain moisture and other nutrients, and controls weeds, thus improving soil health and increasing crop yields. Effects of biodegradable mulch on soil and crops have been studied by several universities. Their results are summarized in Item B.11 and are provided in Appendix E.

Carbon black specifically improves crop yields, as shown in 1916 by Skinner and Beattie. See Appendix E.

Titanium dioxide is an inert mineral found in nature.

10. Safety information about the substance including a Material Safety Data Sheet (MSDS) and a substance report from the National Institute of Environmental Health Studies.

MSDS for carbon black, titanium dioxide, the common monomers and processing aids are attached in Appendix C, along with the EPA Action Memoranda regarding carbon black and titanium dioxide.

11. Research information.

The following research reports are available in Appendix F and are summarized below for biodegradable mulch films tested against the standard black polyethylene (PE) mulching film. Note the evolution of mulch films made with biodegradable resins between 2003 and 2007.

Photodegradable mulches have never been proven to be 100% biodegradable and do not comply with ASTM D6400 or equivalent biodegradation and compostability standards.

Washington State University, Vancouver Research and Extension Unit, Vancouver, Washington – Annual Research Reports 2003-2007.

Research Report 2003: The authors studied six mulch treatments: black polyethylene (PE) plastic (control), biodegradable Garden Bio-Film, a cornstarch-based black film made from the material, Mater-Bi®, and four paper roll mulches. They found no differences in the quality or durability of the six mulch treatments or in the quality and yield of the vegetable crop (basil). The plastic mulch and Garden Bio-Film proved as high in quality as the paper mulches

Research Report 2004: The authors tested 6 materials in 2004 in an organic vegetable production system: black PE plastic control, black Garden BioFilm, 81-lb Kraft brown paper, and three non-degradable mulches. Four vegetables were grown: lettuce, bell peppers, broccoli, and watermelon. There was a significant difference among mulch treatments in the number of days to broccoli harvest, but all other crops were not significantly different. Broccoli was harvested earliest from plots treated with Garden BioFilm, and latest from plots treated with black plastic.

Mean number of days from transplant to harvest.				
Mulch	Lettuce	Broccoli	Peppers	Watermelon
Black Plastic (control)	33.9	75.9	91.2	84.5
Garden BioFilm	33.5	66.9	85.2	83.2
Kraft 81-lb	33.0	67.6	85.8	88.1

Although lettuce yield was not significantly different due to mulch treatments, Kraft 81-lb paper mulch produced the smallest yield. Broccoli yield (kg) and number of heads were significantly greater in the black plastic mulch plots. Garden BioFilm and Kraft 81-lb paper produced large yields as well.

Mean plot yield, average head weight, and number of marketable heads						
	LETTUCE			BROCCOLI		
Mulch	Yield (kg)	Avg head wt. (g)	No. of heads	Yield (kg)	Avg head wt. (g)	No. of heads
Black Plastic	4.98	276	18.0	7.28	655	12.8
Garden BioFilm	5.03	252	19.8	4.78	762	6.3
Kraft 81-lb	4.47	232	19.3	4.68	684	7.0

There were no significant differences in pepper yield (kg), number of fruit and average pepper weight due to the different mulches. However, Garden BioFilm tended to produce the greatest yield (kg) followed by black plastic, while Kraft 81-lb paper produced the lowest yield.

Watermelon yields (kg) were significantly different due to the different mulch treatments. Kraft 81-lb produced the lowest yields and number of fruit. There were no significant differences in average fruit weight; therefore differences in overall yields were due to differences in fruit number.

Mean plot yield, average fruit weight, and number of marketable fruit						
	PEPPER			WATERMELON		
Mulch	Yield (kg)	Avg fruit wt. (g)	No. of fruit	Yield (kg)	Avg fruit wt. (kg)	No. of fruit
Black Plastic	19.48	253	79.0	55.10	3.078	18.8
Garden BioFilm	22.11	270	80.5	47.50	2.953	16.3
Kraft 81-lb	11.23	164	70.5	19.64	2.742	7.0

Conclusions. Results of this study indicate that there are alternatives to the standard plastic mulch that can produce comparable results in crop productivity, soil temperature, and affordability. Fully degradable mulches provide the added incentives of decreased work and decreased disposal costs because they do not have to be removed from the field. Garden BioFilm has been approved for use in organic agriculture[10], and can be tilled into the soil. It produced good results in this study, and its quick and thorough biodegradation may be desirable for short-season crops and immediate tillage into the soil, but the cost of this mulch is high, and its rate of degradation may be too fast for longer-season crops. The paper mulches were less effective in general. Kraft 81-lb paper and Kraft 42-lb coated paper produced similar results in terms of yield and durability, but the Kraft 42-lb coated paper is not degradable and more labor-intensive to remove than black plastic. These results are preliminary, and this study will likely be repeated in 2005.

Research Report 2005: The authors evaluated nine mulches in 2005: black PE plastic, black biodegradable BioFilm, and five new paper products. The mulch products were compared to black plastic (control) and were evaluated for durability, and effects on soil temperature and crop yield on a non-certified field that was managed organically.

Durability: The 5 paper mulch products declined in quality relatively quickly, and were rated 5 or below (50% cover or less) only 5-6 weeks after field application. Weed growth occurred under all the paper mulches and was the major cause of their decline in quality. Weeds grew large enough to push the paper mulches off the ground, causing them to tear and eventually blow away. Weed growth under the paper mulch indicates there was significant light penetration through these products. Garden BioFilm was the least durable mulch in 2004, steadily declining to a final quality rating of 2 (20-29% cover), indicating that it was nearly gone at the end of the growing season. In 2005, Garden BioFilm quality dropped below 50% after 7 weeks in the field, and its quality rating remained slightly better than the paper mulches until 12 weeks after application, at which point it dropped below a rating of 2.

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[10] Garden BioFilm had been accepted by some certifiers at that time, including the WSDA Organic Food Program, since it complies with §205.206(c)(1), “mulching with fully biodegradable materials.”

Yields of all crops were significantly affected by mulch products. Yields in all paper plots were significantly lower due to their general degradation and the subsequent weed growth in those plots. Yield of lettuce was least impacted by mulch product due to its short time to harvest, and paper or cornstarch products may be most suitable for similar short season crops. Garden BioFilm and two non-biodegradable plastic films resulted in the highest overall yield of lettuce both years.

Black plastic mulch resulted in high broccoli yield. Paper products resulted in the lowest broccoli yields. Garden BioFilm mulch was equivalent to black plastic.

Mean marketable yield, average head weight, and number of marketable heads

	LETTUCE			BROCCOLI		
Mulch	Yield (kg)	Avg head wt. (g)	No. of heads	Yield (kg)	Avg head wt. (g)	No. of heads
Black Plastic	4.77	202	19	3.08	280	11.0
Garden BioFilm	5.55	245	19	2.98	270	11.0
Paper LF 1	1.11	92	6	1.57	150	9.8
Paper LF 2	3.04	127	20	2.29	190	11.8
Paper LF 3	3.36	141	17	2.18	210	9.8
Paper LF 4	3.83	180	18	2.59	230	11.3
Planters Paper	3.71	155	19	2.03	170	12.0

All paper products resulted in significantly lower pepper and watermelon yields. The alternate biodegradable plastics resulted in slightly (Garden BioFilm) to substantially greater yields than black plastic for both vegetables.

Mean marketable yield, average fruit weight, and number of marketable fruit

	PEPPER			WATERMELON		
Mulch	Yield (kg)	Avg fruit wt. (g)	No. of fruit	Yield (kg)	Avg fruit wt. (kg)	No. of fruit
Black Plastic	3.56	90	38.75	16.2	1.8	9.0
Garden BioFilm	3.68	90	41.50	20.0	1.5	12.5
Paper LF 1	0.2	40	5.25	1.0	0.6	1.3
Paper LF 2	0.51	60	9.50	4.4	1.1	4.5
Paper LF 3	0.68	80	8.50	0.6	0.5	1.3
Paper LF 4	0.15	30	3.75	3.0	0.8	3.5
Planters Paper	0.06	50	1.25	2.0	0.8	2.3

The authors concluded that Garden Biofilm degrades completely in the soil, but it does not retain its quality long enough to be useful for long season crops. Paper products were suitable for a short season crop such as lettuce, but did not retain their quality for a long season crop such as watermelon. Once mulch cover fell below 50% (a quality rating of 5 or below), the product was ineffective for weed control or temperature modification. The extensive weed growth under all the paper mulch products indicates there was significant light penetration through these products.

Research Report 2006: The authors evaluated 10 alternative mulches in a field study in 2006 on a field managed organically but not certified organic. Two non-biodegradable plastic products, four Garden BioFilm variants, and six paper products were compared to black plastic.

Durability: Black plastic, the other two non-biodegradable plastics, and paper LF 5 were the most durable products, with quality declining by less than 20% over the course of the growing season. Paper mulch LF 4 declined in quality in a similar fashion as in 2005 while Planters Paper was considerably more durable in 2006 than in 2005, indicating a significant variation in performance. In 2006 just as in 2005, weed growth occurred under the LF 4 paper mulch, and this was the primary cause of its decline in quality. The 4 cornstarch mulch products varied from each other in quality over the season, with Garden Biofilm NF01U/P15 being the most durable followed by Garden Biofilm NF803/P15. The Garden Biofilm declined in quality in 2006 in a similar fashion as in 2005.

Yields: Yields with paper mulches tended to be lower than with other mulch products, and these differences were significant for some crops. In general, yield of lettuce and broccoli (both cool season crops) were least impacted by paper mulch whereas yield of pepper and watermelon (both warm season crops) were more greatly impacted. In 2006, only LF 4 degraded early and yields were consequently lower than for other products.

Lettuce yield and number of heads tended to be greater with LF 5, and Garden Biofilm NF803/12 and lower with black plastic, Garden Biofilm, and LF 4. Broccoli yield tended to be greater with Garden Biofilm NF803/15 and Garden Biofilm NF803/12, and lower with LF 5, Planters Paper and black plastic. Numbers of broccoli heads were greater with Garden Biofilm, and lowest with Garden Biofilm NF01U/P15. The average head weight of broccoli was greatest with Garden Biofilm NF803/15 and Garden Biofilm NF803/12, and lowest with black plastic and Garden Biofilm.

Mean plot yield, average head weight, and number of marketable heads						
	LETTUCE			BROCCOLI		
Mulch	Yield (kg)	Avg head wt. (kg)	No. of heads	Yield (kg)	Avg head wt. (kg)	No. of heads
Black Plastic	2.14	135	16	1.18	137	8.3
Garden BioFilm	2.20	125	20	1.29	137	9.5
" NF01U/P 15 mic	2.62	154	17	1.66	258	6.5
" NF803/P 12 mic	2.33	131	18	1.36	234	5.8
" NF803/P 15 mic	2.33	144	16	2.03	318	6.5
Paper LF 4	2.31	142	16	1.25	162	7.8
Paper LF 5	2.73	162	17	1.14	188	6.3
Planters Paper	2.43	154	16	1.15	150	7.8

Pepper yield and number of fruit were greater with Garden Biofilm NF803/15 and lowest with LF 4, Planters Paper and black plastic. Watermelon yield and fruit number were greater with Garden Biofilm NF803/15, and lowest with LF 4 and LF 5. The average fruit weight of watermelon was lowest with LF 5.

Mean marketable yield, average fruit weight, and number of marketable fruit						
	PEPPER			WATERMELON		
Mulch	Yield (kg)	Avg fruit wt. (g)	No. of fruit	Yield (kg)	Avg fruit wt. (kg)	No. of fruit
Black Plastic	1.86	114	15.8	11.4	1.7	6.5
Garden BioFilm	2.67	129	21.0	14.6	1.8	8.3
" NF01U/P 15 mic	2.52	159	18.8	12.7	1.5	8.5
" NF803/P 12 mic	3.01	108	27.8	18.0	1.3	13.8
" NF803/P 15 mic	4.09	119	34.0	18.7	1.7	11.0
Paper LF 4	0.40	107	3.8	1.9	1.3	1.5
Paper LF 5	2.11	111	19.0	6.6	1.1	6.5
Planters Paper	1.51	113	13.8	10.5	1.4	6.8

Research Report 2007: The authors evaluated 8 alternative mulches versus black plastic in a field that was certified organic.

Durability: Mulch products evaluated in this study showed significant differences in quality (durability) over time. Black plastic and two other non-biodegradable plastic mulch films were the most durable mulch. Paper LF 5, the most durable biodegradable product in 2006, with quality declining by less than 20% over the course of the growing season, declined more rapidly in quality in 2007, Black LF5 was slightly lower than regular LF 5 but not significantly so. Weed growth under the LF 4 paper mulch in 2006 was the primary cause of its decline in quality. Planters paper had relatively good durability in 2006 while in 2007 durability was low. Of the corn starch products, Garden Biofilm NF01U/P15 and Garden Biofilm NF803/P15 were the most durable both years while Garden Biofilm NF803/P12 and Garden Biofilm were the least durable.

In 2007, there was little difference in crop yield due to mulch product. Yield, number of heads and head weight of lettuce and broccoli were not significantly affected by mulch product. Pepper yield was greatest with black plastic, Garden Biofilm NF01U/P15, Garden BiofilmNF803/15, and Garden Biofilm803/12, and lowest with Black LF 5, LF 5, Planters Paper, and Garden Biofilm. Watermelon yield was not impacted by mulch product, most likely due to overall low pollination in this crop throughout all plots.

Mean marketable yield (kg)				
Mulch	lettuce	broccoli	pepper	watermelon
Black Plastic	9.14	7.35	8.01	15.30
Garden BioFilm	8.60	7.30	5.12	8.90
" NF01U/P 15 mic	10.90	7.41	5.69	13.90
" NF803/P 12 mic	10.21	7.54	6.47	11.50
" NF803/P 15 mic	8.67	7.10	5.85	7.40
Paper LF 5	9.07	7.52	4.29	
Black Paper LF 5	8.56	6.50	3.54	
Planters Paper	8.61	7.23	4.83	

The authors concluded that once mulch coverage fell below 50%, the product was ineffective for weed control. Both years Garden Biofilm and Garden Biofilm NF803/P12 reached a rating of 5 by early August while all other degradable mulch products reached a rating of 5 by early to mid September in one year only. Preliminary results indicated that LF 5 was the most durable of all alternative mulches tested. However, durability was significantly lower in the second year of this study (2007). Of the cornstarch products, Garden Biofilm NF01U/P15 and Garden Biofilm NF803/P15 appeared somewhat durable in the field and had the added benefit of resulting in high crop yields.

According to the authors, a degradable mulch ideally would degrade in the soil, eliminating the removal and disposal costs. In this study, cornstarch and paper mulches were tilled into the soil at the end of the season and, by the following spring, they had broken down to the point where residues were no longer visible to the naked eye.

SARE project FNE 05-562 - 2005
AgroFilm (BioBag), made from the material, Mater-Bi®, showed comparable yields and nearly the same costs as plastic mulch for two out of the three crops the authors experimented with. Their results favored black plastic for melons. More experiments with other types of crops and other types of materials are needed so farmers can confidently switch from plastic mulch to a biodegradable material. In the meantime, these authors stated they would switch to Agrofilm for many of their crops in 2006 (but not for melons) and hoped to reduce the amount of plastic waste generated at the farm.

Rangarajan and Leonard (2007) found in 2006 field trials that field application of Mater-Bi® was similar to black plastic. The products had excellent stretch and soil temperatures were similar early in the season. Mid season plant fresh weights indicate that growth on Mater-Bi® mulches was similar to black plastic. All Mater-Bi® products were starting to break down (areas exposed to direct sunlight) at the end of July. Despite some early breakdown, they found no differences in early or total yield with any of the different colors of biodegradable mulch and black plastic mulch. Average fruit size and weight (4.0 lbs) were similar among mulch treatments.

Guerrini et al. (2008) described their preliminary trials of biodegradable mulch (Mater-Bi® mulch films) in an organic vineyard at the 16th IFOAM Organic World Congress. Some biodegradable mulch films were able to reduce the growth of weeds for a period of 12 months. Film thickness and formulation play an important role in the efficiency of long-lasting biodegradable mulch films. From the budding stage until the end of the vegetative cycle, the development of mulched vines was higher compared to vines without mulching. This greater growth may be a result of a faster soil warming in spring (due to the black color of the films), higher water retention, and a reduction in weed competition.

Minuto et al. (2008) also described their use of biodegradable mulching in vegetable production at the 16th IFOAM Organic World Congress. Trials were carried out in Liguria during three years (2004-2006) to evaluate the use of starch-based bioplastics for soil mulching. All trials carried out in the open field as well as in the greenhouse on different vegetable crops demonstrated the effectiveness of biodegradable films in controlling weeds and in increasing yield. The use of biodegradable mulching films permitted compliance with integrated production regulations set up by the regional authority and it is potentially adoptable in an organic farming context.

Orzolek (2008) found that the PHA (polyhydroxyalkanoate) films comprising PHB (poly-2-hydroxybutyrate) were very well suited for agricultural mulch film applications.

Moreno et al. (2009) compared the effect of three mulches, black polyethylene, black biodegradable corn starch plastic and aluminized photodegradable plastic on a tomato crop in an open field. They measured mulch deterioration, soil temperature under mulches, tomato yield and fruit quality attributes (total soluble solids, firmness, dry weight, juice content and shape).

Biodegradable mulch performed its function successfully and disappeared visually from the soil about three months after the crop was finished. Photodegradable mulch deteriorated prematurely and polyethylene film was practically intact at the end of season. Significant differences in mean soil temperature under mulches were observed (27.8ºC in biodegradable, 28.7ºC in aluminized and 31.8ºC in polyethylene), although they did not have a marked effect on the crop yield. Marketable yields were similar in both biodegradable and polyethylene mulches (9.82 and 8.66 kg m-2, respectively), and higher than those recorded in aluminized photodegradable mulch (6.85 kg m-2), which resulted in the highest sunscald in fruits. No effect on the fruit quality attributes was observed. They concluded that biodegradable plastic mulches could be a good alternative to the traditional plastic films and that aluminized photodegradable mulches seem not very advisable because they reduce marketable yield and could increase the incidence of sunscald.

Two publications from Penn State Extension agent Dupont summarized their experience and that of other research stations with biodegradable mulches, as follows:

Mater-bi Agromulch (Biotelo) – Novamont
Agrofilm – biobag

- Corn starch base
- Compostable
- Approved for use by IFOAM (European Organic)

<u>Notes Rangarajan 2006</u>

- Field application similar to plastic
- Good soil stretch
- Soil temperature similar to plastic
- Similar yields to plastic for muskmelon
    - Total T/A[11] – 14 (plastic), 13 (Biobag), 12.2 (Mater-bi), 15 (Mater-bi brown)
    - Early Season T/A – 3.5 (plastic) vs 1.6-2.8 (biodegradables)

<u>Notes from Cave Moose Farm SARE Project</u>

- “The material began to degrade by mid-summer. . .(but) the ground underneath remained bare.”
- Yield per dollar spent was better with plastic for winter squash but higher with Agrofilm for pumpkins.

<u>Notes from Orzolek 2007, 2008</u>

- Biodegradable performed as good or better than plastic for yields in pepper, cantaloupe, eggplant, zucchini (i.e. 30-40 lb peppers/ 24 ft).
- No weed growth/ competition when film degraded before crop matured.

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[11] T/A = total cost per acre (includes removal and disposal costs for black plastic mulch.

Metabolix

- Resins from plant derived sugars
- Experimental films #7, #13, #19 (black), #23 (clear)

<u>Notes from Orzolek 2009</u>

- New mulches are more flexible and did not tear.
- Did not start to degrade until 14 days after application.
- Brittle pieces tended to blow off site.
- Pepper, cantaloupe and acorn squash produced lower yields on biodegradable (Metabolix).
- Even after biodegradable plastic began to break down, no weeds were seen on the bed.
- Incorporation of the remaining mulch by roto-tilling increased degradation.

In contrast, paper-based biodegradable mulch was less satisfactory.

WeedGuard Plus – Non Fert - Sunshine Paper Co

- OMRI listed
- Weed Guard Plus – Fert contains 5-5-5

<u>Notes from Orzolek 2008</u>

- Paper tore when press wheels were angled.
- Paper dried and stayed intact after rain.
- Soil temp 2" deep (Jul14) was 84 F vs. 79 F under black non-degradable plastic.
- Yield compared to non-degradable plastic
    - Cantaloupe was the same (32/ 27 lbs vs. 42 lbs/ 100 ft).
    - Acorn squash was 36% higher with paper + 5-5-5.
    - Pepper yield was lower (18-21 vs. 38 fruit/ 100 ft).
    - Eggplant yield was lower (14/21 vs. 34 fruit/ 100 ft).

<u>Notes from Cave Moose Farm SARE Project</u>

- Cost per ft including materials and labor for laying, maintaining, removing and disposing
    - $0.34 – 0.35/ ft paper
    - $0.19-0.20/ ft Agrofilm
    - $0.20-$.21/ ft plastic

12. "Petition Justification Statement'' for Inclusion of Biodegradable Mulch Film Made from Bioplastics on the National List at §205.601.

The development of polyethylene as a plastic film in 1938 and its subsequent introduction as a plastic mulch in the early 1950s revolutionized the commercial production of selected vegetable crops. Throughout the succeeding years, research, extension, and industry personnel, together with growers, have documented the advantages of using plastic mulch as one component of a complete "intensive" vegetable production system. Although a variety of vegetables can be grown successfully using plastic mulches, muskmelons, honeydews, watermelons, squash, cucumbers, tomatoes, peppers, eggplant, okra, sweet corn, and cole crops have shown significant increases in earliness, total yield, and quality. Research continues on field evaluation of new formulations of degradable, wavelength-selective, and colored plastic mulches and on cropping systems to use best these specific improvements. The use of plastic mulches for the production of vegetable crops continues to increase throughout the United States and the world.[12]

When the OFPA was enacted on November 28, 1990, the universal plastic mulch in the United States was polyethylene plastic, a petroleum-based material. In order to address the fact that this plastic is from a synthetic, non-renewable resource, and does not break down in the soil or enrich the soil, OFPA included Sec. 2109(c)(2) [7 U.S.C. 6509]: "(c) Crop Management. For a farm to be certified under this title, producers on such farm shall not – (2) use plastic mulches, unless such mulches are removed at the end of each growing or harvest season."

Polyethylene is a polymer joined by carbon-to-carbon bonds, which are resistant to biological digestion by almost all organisms and their enzymes, because there is no other functional group on the polyethylene chain that would give the enzyme 'purchase' so it could do its work. In contrast, the bioplastics being petitioned are polyesters, polymers formed by the reaction of a hydroxyl group and a carboxyl group. The natural world is full of ester linkages. Living cells and organisms have developed enzymes to hydrolyze the ester linkage. Examples of natural esters are fats and oils, where three fatty acid molecules are esterified to glycerol/glycerin; natural waxes, where long-chain alcohols are esterified to a fatty acid; and some natural flavors, such as banana flavor, n-amyl acetate, an ester of n-amyl alcohol and acetic acid

At the First International Conference on Soil Solarization held in Amman, Jordan, 19-25 February 1990, a paper on soil solarization[13] delivered by American scientists contained the following text: "**Only flexible PVC and PE films are suitable for mulching.** Theoretically, PVC should prove better in cases where an increase in soil temperature is a decisive requirement. However, in practice, the difference in recorded temperature under PVC and PE mulch is not significant. Therefore, PE is generally preferred because of its lower price and greater permeability to long-wave infrared radiation which results in a greater amount of radiation flowing from the soil to the aerial parts of plants during the night (26)."

In 1995, the World Bank published Technical Paper 253, "Protected Agriculture – A Global Review," authored by M. H. Jensen and A. J. Malter. The nature of the plastic mulch in use in the world at that point in time is described on page 13 of this reference work. "The material being used for mulch film is mostly low density polyethylene (LDPE) but some LLDPE (extra low density) and high density polyethylene (HDPE) is also used. Generally, LDPE film is 0.014 mm; however, film made of LLDPE, HDPE and LDPE mixed with HDPE along with LLDPE mixed with HDPE is only 0.008 to 0.01 mm thick. The very thin films are very popular with the growers,

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[12] Plastic Mulches for the Production of Vegetable Crops. William James Lament, Jr. HortTechnology Jan./Mar. 1993 3(1) 35-39.

[13] http://www.fao.org/docrep/T0455E/T0455E00.htm; Accessed March 2, 2011.

since the growth benefits of the thin mulch are the same as the 0.014 mm ones and cost 30 percent less. Most of the mulch films are clear although some silver, black, and white films are used."

The U.S. bible for organic vegetable growing, "Rodale's All-New Encyclopedia of Organic Gardening – The Indispensable Resource for Every Gardener," published in 1992 by Rodale Press, described "mulch" as follows (pages 391-2):

> "There are two basic kinds of mulch: organic and inorganic. Organic mulches include formerly living material such as wood chips, shredded bark, chopped leaves, straw, grass clippings, compost, sawdust, pine needles, and even paper. Inorganic mulches include gravel, stones, black plastic, and geotextiles (landscape fabrics).
>
> "Both types discourage weeds, but organic mulches also improve the soil as they decompose. Inorganic mulches don't break down and enrich the soil, but under certain circumstances they're the mulch of choice. For example, black plastic warms the soil and radiates heat during the night, keeping heat-loving vegetables such as eggplant and tomatoes cozy and vigorous."

Unfortunately, polyethylene plastic mulch has two major problems: removal and disposal. A major problem with plastic mulch is removal from the field after cropping (Stall and Bryan, 1981). Plastics have been disposed of routinely by burning, burial, or dumping in landfills. The growing environmental concerns over disposal of plastic mulches by burning and dumping in landfills led to restrictions in some regions (Ennis, 1987).

The problems of polyethylene plastic removal and disposal stimulated research and development on biodegradable mulch films with equivalent efficacy to polyethylene plastic mulch. Lament (1992) described the state of affairs in 1992:

> "In the early 1960s, photo- or biodegradable plastic was recognized as one solution to the disposal problem associated with plastic mulches. Work on biodegradable starch-based film (Otey and Westoff, 1980) and photodegradable polyolefin polymer and polyethylene copolymer films (Carnell, 1980; Ennis, 1987) has been underway since the 1960s; however, resulting mulches have been quite variable in their rate of degradation (Chu and Matthews, 1984; Wien, 1981). Recently, newer photodegradable products (Optigro, Leco Industries, Inc., Quebec, Canada; Biolan, CT Films, Schaumburg, Ill.; and Plastigone, Miami, Fla.) have shown more-satisfactory degradation characteristics when tested in different regions of the country (Clough and Reed, 1989; Johnson, 1989; Kostewicz and Stall, 1989; Sanders et al., 1989; Wolfe, 1989). Other options to the plastic mulch disposal problems are retrieval and recycling or incineration/energy reclamation for the BTUs locked inside the plastic mulch."

The culmination of this half-century of research and development is the biodegradable mulch films that are the subject of this petition. The restriction within OFPA to remove plastic mulch at the end of each growing or harvest season should not be applicable to biodegradable films because by definition and intention, a biodegradable mulch film is substantially biodegraded by the end of the growing season or by the beginning of the following growing season, so its removal would be difficult and may be physically impossible.

The removal and disposal issues with polyethylene plastic mulch have increased since passage of OFPA. In 1999, more than 30 million acres of agricultural land worldwide were covered with plastic mulch, and those numbers have increased significantly since then. Many organic vegetable farmers rely on black plastic mulch. Unfortunately, black polyethylene plastic mulch is made from a non-renewable resource and has a major disposal issue. At the end of the crop year, the plastic must be pulled and thrown out, which adds trash to landfills, takes a lot of time, and delays cover cropping. There is estimated to be 100-120 lb/acre of un-recyclable, petroleum-based waste that farmers must pay to landfill at season's end (Grantham, 2011). With the recent trend toward "going green", researchers are seeking environmentally friendlier alternatives to conventional plastic mulch (ScienceDaily, Feb. 26, 2009).

The use of black polyethylene plastic film is fundamentally antithetical to the notion of sustainable agriculture and organic agriculture. The USDA's SARE program (Sustainable Agriculture Research and Education) has provided several grants to conduct comparisons of biodegradable mulches to black plastic mulch. In 2006, Laura Sorkin, an organic farmer and researcher, completed SARE project FNE 05-562. The conclusion of her study stated; "Both conventional and organic farmers rely on plastic mulch to control weeds, heat the soil and retain nutrients. While it is very effective in all these areas, there is concern over the amount of waste generated when the plastic is pulled out of the fields at the end of the season. Using large quantities of a petroleum-based product that cannot be recycled is antithetical to the principles of sustainable farming. Even if a farmer chose to switch half of her crops over to biodegradable mulch, this would certainly have a positive effect on reducing agricultural pollution and use of non-renewable resources."

Mulching has three objectives: controlling weeds, modulating soil temperature, and retaining moisture and other nutrients. Current alternatives are:

- Mulching with black polyethylene plastic, a synthetic allowed at §205.601(b)(2)(ii)
- Mulching with newspaper or other recycled paper, without glossy or colored inks, allowed at §205.601(b)(2)(i)
- Mulching with cover crops
- Mulching with straw, leaves and/or other natural degradable materials

In 2010, the Rodale Institute received a Northeast SARE grant to find alternatives to using non-degradable black polyethylene plastic in vegetable production and started promoting a campaign called "Escape from Black Plastic!" Their website quotes, "Black plastic mulch does many things well for vegetable farmers, but its cost, disposal issues and environmental downsides continue to drive research into cover crop mulches that achieve the good without so much bad." (Grantham, 2011)

Mulching with cover crops is at the center of the Rodale SARE grant. Although cover crops, such as clover between orchard rows is a common practice, the Rodale study looks at rye, vetch and combinations of these types of crops that are grown between harvests of vegetables, such as tomatoes, pumpkins, squash, and cabbage, as part of the rotation and then cut and left as mulch. Cover crops have long helped organic farmers mitigate environmental damage and increase productivity, from suppressing weeds without herbicides to improving soil structure to diminish water runoff. They require more management and uncertainty than laying down plastic, but contribute to long-term biological improvement rather than landfill trash. Herbicides, though, are still often required to achieve adequate weed control. In addition, weeds were found to quickly break through the mowed or chopped residue requiring the use of a new tool, the roller-crimper. The roller-crimper not only terminates the cover crops by flattening and crushing, but also leaves them in an intact mat that is better able to suppress weeds throughout the season.

Another challenge is planting in the cover crop mulch. Seeding is not practical and even to hand transplant into the soil under the mulch is best done when the soil is moist either from recent rain or irrigation. According to one of the farmers participating in the Rodale trials, “it could be like trying to hack into concrete with a hand trowel.”[14]

Cover crops as mulch pose challenges for farms that use seed rather than transplants; do not have the equipment needed to cut, roll and crimp the cover crops; do not have topography that would allow use of such equipment; or have intensive, small-scale, diverse mixed vegetable operations.

Mulching with straw, leaves and/or other natural degradable materials applied thick enough to form a dense mat can be effective weed suppressors. As these materials degrade they contribute to soil tilth and fertility. Access to sufficient amounts of material to build a dense mat is often a challenge, as well as the labor involved in applying these materials. Straw and other natural degradable materials may introduce weed seeds and provide an environment that encourages slugs, flea beetles and other pests that could compromise the productivity of the crops and increase the use of pesticides.

The biodegradable mulch films that are the subject of this petition do not have these disadvantages.

13. A Confidential Business Information Statement

This petition contains no Confidential Business Information.

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[14] http://www.rodaleinstitute.org/20111023_growing-vegetables-with-cover-crop-mulch

Appendices

Petition for addition of the Biodegradable Mulch Film Made From Bioplastics to the National List at §205.601(b) as a synthetic substance allowed for use in organic crop production.

Appendix A Authoritative Specification for Biodegradability of Bioplastics in Soils

- Abstract - ASTM Standard D5988: *Standard Test Method for Determining Aerobic Biodegradation in Soil of Plastic Materials or Residual Plastic Materials After Composting*
- Abstract - ASTM Standard D6400: *Standard Specification for Compostable Plastics*
- Abstract - ASTM Standard D6868: *Standard Specification for Labeling of End Items that Incorporate Plastics and Polymers as Coatings or Additives with Paper and Other Substrates Designed to be Aerobically Composted in Municipal or Industrial Facilities*
- Abstract - European Standard EN 13432: *Requirements for packaging recoverable through composting and biodegradation*
- Abstract - European Standard EN 14995: *Requirements for plastics recoverable through composting and biodegradation*
- Abstract - ISO Standard 17088: *Specifications for compostable plastics*
- Abstract - ISO Standard 17556: *Plastics — Determination of the ultimate aerobic biodegradability in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved*
- AIB Vinçotte OK Biodegradable Soil – *Program OK 10 Bio-products-degradation in soil*

Appendix B U.S. Patents and Patent Application describing Manufacture of Biodegradable Plastics

- U.S. Patent No. 6,787,613
- U.S. Patent No. 7,067,596
- U.S. Patent No. 6,096,809
- U.S. Patent Application Publication No. US 2008/0275208

Appendix C Safety and Toxicity Reports

MSDS – Carbon Black

EPA Action Memorandum regarding Carbon Black

MSDS – Titanium Dioxide

EPA Action Memorandum regarding Titanium Dioxide

MSDS – Lactic Acid

MSDS – Adipic Acid

MSDS – Azelaic Acid

MSDS – Terephthalic Acid

MSDS – 1,4-Butanediol

MSDS – Erucamide

MSDS – Glycerin

MSDS - Stearamide

Appendix D Labels of Biodegradable Mulch Film Made From Bioplastics

BIONOV B Biodegradable Mulch Film made with Mater-Bi®

BioTelo Biodegradable Mulch Film made with Mater-Bi®

Appendix E Research Reports – Carbon Black

- Skinner, J.J., and Beattie, J.H. 1916. A study of the action of carbon black and similar absorbing materials in soils. Soil Science, 2(1) 93-101
- John V. Accorsi (1999). The impact of carbon black morphology and dispersion on the weatherability of polyethylene. Presented at the International Wire & Cable Symposium, Atlantic City, November 18, 1999
- Cheng, C.-H., Lehmann, J. and Mark H. Engelhard, M.H. 2008. Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence. Geochimica et Cosmochimica Acta 72: 1598–1610.

Appendix F Research Reports – Field Testing of Biodegradable Mulch Films

- Table describing agricultural mulch films studied at Washington State University
- Miles, C., Garth, L., Sonde M., and Nicholson, M. 2003. Searching for Alternatives to Plastic Mulch . Washington State University; Vancouver Research and Extension Unit, Research Report 2003.

- Miles, C., Becker, G., Kolker, K., Adams, C., Nickel, J., and Nicholson, M. 2004. Alternatives to Plastic Mulch for Organic Vegetable Production. Washington State University; Vancouver Research and Extension Unit, Research Report 2004.
- Miles, C., Kolker, K., Reed, J., and Becker, G. 2005. Alternatives to Plastic Mulch for Organic Vegetable Production. Washington State University; Vancouver Research and Extension Unit, Research Report 2005.
- Miles, C., Reed, J., Klingler, E., Nelson, L., Smith, T., Kolker, K., and Cross, C. 2006. Alternatives to Plastic Mulch in Vegetable Production Systems. Washington State University; Vancouver Research and Extension Unit, Research Report 2006.
- Miles, C., Klingler, E., Nelson, L., Smith, T., and Cross, C. 2007. Alternatives to plastic mulch in vegetable production systems. Washington State University; Vancouver Research and Extension Unit, Research Report 2007.
- Sorkin, L. 2006. A comparison of biodegradable mulches to black plastic mulch. 2006 Final Report. SARE Project Number: FNE05-562.
- Rangarajan, A. and Leonard, B. 2007. Biodegradable mulches: How well do they work? Department of Horticulture, Cornell University.
- Guerrini, S., Martellucci, R., Nardi, G., Ranghino, F., and Bonanzinga, M. 2008. Preliminary Trials in Organic Vineyard with Mater-Bi® Mulch Films. Presented at 16th IFOAM Organic World Congress, Modena, Italy, June 16-20, 2008.
- Minuto, G., Guerrini, S., Versari, M., Pisi, L., Tinivella, F., Bruzzone, C., Pini, S., and Capurro, M. 2008. Use of biodegradable mulching in vegetable production. Presented at 16th IFOAM Organic World Congress, Modena, Italy, June 16-20, 2008.
- Orzolek, M.D. 2008. The effectiveness of biodegradable poly(hydroxy butanoic acid) copolymers in agricultural mulch film applications. Department of Horticulture, Pennsylvania State University, State College, PA.
- Moreno, M. M., Moreno, A., and Mancebo, I. 2009. Comparison of different mulch materials in a tomato (Solanum lycopersicum L.) crop. Spanish Journal of Agricultural Research 7(2), 454-464.
- Dupont, T. 2010. Biodegradable Mulches. The Vegetable & Small Fruit Gazette – Penn State Extension. September 2010. http://extension.psu.edu/vegetable-fruit/newsletter/2010-issues/september-2010-the-vegetable-small-fruit-gazette
- Dupont, T. undated. PennState Factsheet: Degradable Mulches.

ASTM D5988 - 03
Standard Test Method for Determining Aerobic Biodegradation in Soil of Plastic Materials or Residual Plastic Materials After Composting

Significance and Use

The degree and rate of aerobic biodegradability of a plastic material in the environment determines the extent to which and time period over which plastic may be mineralized. Disposal is becoming a major issue with the increasing use of plastics, and the results of this test method may permit an estimation of the degree of biodegradability and the time period over which plastics will remain in an aerobic soil environment. This test method determines the degree of aerobic biodegradation by measuring evolved carbon dioxide as a function of time that the plastic is exposed to soil.

Soil is an extremely species-rich source of inoculum for evaluation of the biodegradability of plastics in the environment. When maintained appropriately with regard to moisture content and oxygen availability, the biological activity is quite considerable, although lower than other biologically active environments, such as activated sewage-sludge or compost. Soil is also the application target for composted materials, and therefore the biodegradability of such materials should be evaluated in the soil environment after the materials have been composted. A mixture of soil and mature compost containing composted plastic material (as obtained after performing Test Method D 5338) is therefore also an appropriate matrix for evaluation of the biodegradability of plastics.

1. Scope

1.1 This test method covers determination of the degree and rate of aerobic biodegradation of synthetic plastic materials (including formulation additives that may be biodegradable) in contact with soil, or a mixture of soil and mature compost, under laboratory conditions.

1.2 This test method is designed to rate the biodegradability of plastic materials relative to a standard in an aerobic environment.

1.3 This test method is designed to be applicable to all plastic materials that are not inhibitory to the bacteria and fungi present in soil and compost.

1.4 The values stated in SI units are to be regarded as the standard.

1.5 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. A specific hazard statement is given in Section 8.

1.6 This ASTM test method is equivalent to ISO 17556:2003.

2. Referenced Documents

The documents listed below are referenced within the subject standard but are not provided as part of the standard.

ASTM Standards
D425 Test Method for Centrifuge Moisture Equivalent of Soils
D618 Practice for Conditioning Plastics and Electrical Insulating Materials for Testing
D883 Terminology Relating to Plastics
D1193 Specification for Reagent Water
D1293 Test Methods for pH of Water
D1898 Practice for Sampling of Plastics
D2980 Test Method for Volume Weights, Water-Holding Capacity, and Air Capacity of Water-Saturated Peat Materials
D2989 Test Method for Acidity-Alkalinity of Halogenated Organic Solvents and Their Admixtures
D4129 Test Method for Total and Organic Carbon in Water by High-Temperature Oxidation and Coulometric Detection
D4972 Test Method for pH of Soils
D5338 Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions
D5511 Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under High-Solids Anaerobic-Digestion Conditions

APHA-AWWA-WPCF Standards
2540 G Total, Fixed, and Volatile Solids in Solids and Semi-Solid Samples

ISO Standard
ISO17556:2003 Plastics--Determination of the Ultimate Aerobic Biodegradability of Plastic Materials in Soil by Measuring the Oxygen Demand in a Respirometer or the Amount of Carbon Dioxide Evolved

ASTM D6400 - 04
Standard Specification for Compostable Plastics

Abstract

This specification covers plastics and products made from plastics that are designed to be composted in municipal and industrial aerobic composting facilities. The properties in this specification are those required to determine if plastics and products made from plastics will compost satisfactorily, including biodegrading at a rate comparable to known compostable materials. The purpose of this specification is to establish standards for identifying products and materials that will compost satisfactorily in commercial and municipal composting facilities.

1. Scope

1.1 This specification covers plastics and products made from plastics that are designed to be composted in municipal and industrial aerobic composting facilities.

1.2 This specification is intended to establish the requirements for labeling of materials and products, including packaging made from plastics, as "compostable in municipal and industrial composting facilities."

1.3 The properties in this specification are those required to determine if plastics and products made from plastics will compost satisfactorily, including biodegrading at a rate comparable to known compostable materials. Further, the properties in the specification are required to assure that the degradation of these materials will not diminish the value or utility of the compost resulting from the composting process.

1.4 The following safety hazards caveat pertains to the test methods portion of this standard: This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate health and safety practices and to determine the applicability of regulatory limitations prior to use.

Note 1—No equivalent ISO specifications exist for this standard.

2. Referenced Documents

The documents listed below are referenced within the subject standard but are not provided as part of the standard.

<u>ASTM Standards</u>
D883 Terminology Relating to Plastics
D5338 Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions
D6002 Guide for Assessing the Compostability of Environmentally Degradable Plastics

<u>Organization for Economic Development (OECD) Standard</u>
OECDGuideline208 Terrestrial Plants, Growth Test

<u>Comite Europeen de Normalisation (CEN)</u>
EN13432 Requirements for Packaging Recoverable through Composting and Biodegradation--Test Scheme and Evaluation Criteria for the Final Acceptance of Packaging

<u>ISO Standard</u>
ISO16929 Plastics--Determination of the Degree of Disintegration of Plastic Materials under Defined Composting Conditions in a Pilot-Scale Test

<u>U.S. Government Standard</u>
40CFR Part 503.13 Standards for the Use or Disposal of Sewage Sludge

<u>Canadian Government Standard</u>
Trade Memorandum T-4-9 Standards for Metals in Fertilizers and Supplements

ASTM D6868 - 11
Standard Specification for Labeling of End Items that Incorporate Plastics and Polymers as Coatings or Additives with Paper and Other Substrates Designed to be Aerobically Composted in Municipal or Industrial Facilities

Abstract

This specification establishes the requirements for labelling of materials and products (including packaging), wherein a biodegradable plastic film or coating is attached (either through lamination or extrusion directly onto the paper) to compostable substrates and the entire product or package is designed to be composted in municipal and industrial aerobic composting facilities. This specification, however, does not describe the contents of the product or their performance with regards to compostability or biodegradability. In order to compost satisfactorily, the product must demonstrate each of the three characteristics as follows: (1) proper disintegration during composting; (2) adequate level of inherent biodegradation; and (3) no adverse impacts on the ability of composts to support plant growth.

1. Scope

1.1 This specification covers end items that include plastics or polymers where plastic film/ sheet or polymers are incorporated (either through lamination, extrusion or mixing) to substrates and the entire end item is designed to be composted under aerobic conditions in municipal and industrial composting facilities, where thermophilic temperatures are achieved.

1.2 This specification is intended to establish the requirements for labeling of end items which use plastics or polymers as coatings or binders, as "compostable in aerobic municipal and industrial composting facilities."

1.3 The properties in this specification are those required to determine if end items (including packaging) which use plastics and polymers as coatings or binders will compost satisfactorily, in large scale aerobic municipal or industrial composting where maximum throughput is a high priority and where intermediate stages of plastic biodegradation should not be visible to the end user for aesthetic reasons.

1.4 The following safety hazards caveat pertains to the test methods portion of this standard: This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate health and safety practices and to determine the applicability of regulatory limitations prior to use.

Note 1—There is no known ISO equivalent for this standard.

2. Referenced Documents

The documents listed below are referenced within the subject standard but are not provided as part of the standard.

<u>ASTM Standards</u>
D883 Terminology Relating to Plastics
D3715/D3715M Practice for Quality Assurance of Pressure-Sensitive Tapes
D5338 Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions
D6002 Guide for Assessing the Compostability of Environmentally Degradable Plastics
D6400 Specification for Compostable Plastics
D6866 Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis

<u>Organization for Economic Development (OECD) Standard</u>
OECDGuideline208 Terrestrial Plants, Growth Test

<u>Comite Europeen de Normalisation (CEN)</u>
EN13432 Packaging-Requirements for Packaging Recoverable through Composting and Biodegradation-Test Scheme and Evaluation Criteria for the Final Acceptance of Packaging

<u>ISO Standards</u>

<u>Government Standard</u>
40CFR Part 503.13 Standards for the Use or Disposal of Sewage Sludge

EN 13432:2000
Packaging. Requirements for packaging recoverable through composting and biodegradation. Test scheme and evaluation criteria for the final acceptance of packaging

Abstract

This European Standard specifies requirements and procedures to determine the compostability and anaerobic treatability of packaging and packaging materials by addressing four characteristics: 1) biodegradability; 2) disintegration during biological treatment; 3) effect on the biological treatment process; 4) effect on the quality of the resulting compost. In case of a packaging formed by different components, some of which are compostable and some other not, the packaging itself, as a whole is not compostable.

EN 14995:2006
Plastics. Evaluation of compostability. Test scheme and specifications

Abstract

This European Standard specifies requirements and procedures to determine the compostability or anaerobic treatability of plastic materials by addressing four characteristics: I) biodegradability, II) disintegration during biological treatment, III) effect on the biological treatment process and IV) effect on the quality of the resulting compost. NOTE For packaging EN 13432 applies.

ISO 17088:2008
Specifications for compostable plastics

Abstract

ISO 17088:2008 specifies procedures and requirements for the identification and labelling of plastics, and products made from plastics, that are suitable for recovery through aerobic composting. The four following aspects are addressed:

1. biodegradation;
2. disintegration during composting;
3. negative effects on the composting process and facility;
4. negative effects on the quality of the resulting compost, including the presence of high levels of regulated metals and other harmful components.

This specification is intended to establish the requirements for the labelling of plastic products and materials, including packaging made from plastics, as “compostable” or “compostable in municipal and industrial composting facilities” or “biodegradable during composting” (for the purposes of this International Standard, these three expressions are considered to be equivalent). The labelling will, in addition, have to conform to any international, regional, national or local regulations (e.g. European Directive 94/62/EC).

ISO 17556:2003
Plastics -- Determination of the ultimate aerobic biodegradability in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved

Abstract

ISO 17556:2003 specifies a method for determining the ultimate aerobic biodegradability of plastic materials in soil by measuring the oxygen demand in a closed respirometer or the amount of carbon dioxide evolved. The method is designed to yield an optimum degree of biodegradation by adjusting the humidity of the test soil.

If a non-adapted soil is used as an inoculum, the test simulates the biodegradation processes which take place in a natural soil environment; if a pre-exposed soil is used, the method can be used to investigate the potential biodegradability of a test material.

This method applies to the following materials:

1. Natural and/or synthetic polymers, copolymers or mixtures of these.
2. Plastic materials which contain additives such as plasticizers or colorants.
3. Water-soluble polymers.
4. Materials which, under the test conditions, do not inhibit the activity of the microorganisms present in the soil. Inhibitory effects can be measured using an inhibition control or by another suitable method (see e.g. ISO 8192). If the test material inhibits the microorganisms in the soil, a lower test material concentration, another type of soil or a pre-exposed soil can be used.

VINCOTTE – CERTEST PRODUCTS

OK Biodegradable SOIL : Initial acceptance tests

Doc Ref : **OK10-E** Edition : B [1]
Application Date : 2001-09-27 Page : 1 / 2
Replace : OK10-A

Program OK 10

Bio products – degradation in soil

I. Applicable specifications :

* European standard reference EN 13432 (2000)
* European standard reference EN 29408 (1993)
* European standard reference EN 29439 (1993)
* International draft standard with reference ISO DIS 17566.2 (2001)
* International standard with reference ISO 11266 (1994)
* International standard with reference ISO 14851 (1999)
* International standard with reference ISO 9408 (1991)
* International standard with reference ISO 14852 (1999)
* International standard with reference ISO 9439 (1990)
* American standard with reference ASTM D.5988-96 (1996)
* American standard with reference ASTM D.5271-92 (1992)
* American standard with reference ASTM D.5209-92 (1992)
* Document with reference OECD 301 C (1993)
* Document with reference OECD 301 B (1993)
* Document with reference OECD #208 (1993)

II. Documents to be supplied :

* Description of the product to be certified. This includes:
  - Used constituents
  - If available, fingerprint analyses (e.g. IR or X-ray analyses)
* Identification of the manufacturer and meaning of the codes used
* Manufacturing specification and grounds for refusal
* Available reports,...

III. Classification :

None.

IV. Examinations and tests - particular modalities :

A) Preliminary examinations

1. Study of the file and preliminary inspection of the state of the presented product.
2. Verification of the clarity of the instructions for use and the storage modalities

B) General test programme

B.1. Chemical characteristics

The heavy metals must be below following limits. These are based on European standard for compostability (EN 13432) which themselves are based on 50% of the criteria for the Community eco-label for soil improvers (EC OJL, 219, 7.8.98, p. 39).

Zn	150	Cr	50
Cu	50	Mo	1
Ni	25	Se	0.75
Cd	0.5	As	5
Pb	50	F	100
Hg	0.5		

B.2. Biodegradation

To be eligible for "OK Biodegradable SOIL" certification, materials or products shall be inherently and ultimately biodegradable as demonstrated in laboratory tests.

<u>Tests</u>

The preferred type of biodegradation test is a soil biodegradation test according to ISO DIS 17566.2, ISO 11266 or ASTM D.5988-96.

Alternatively, also an aquatic, aerobic biodegradation test can be used with the prerequisite that these tests are executed at ambient temperature (20-25°C). Standards : ISO 14851, ISO 9408, OECD 301 C, ASTM D.5271-92, EN 29408, ISO 14852, ISO 9439, OECD 301 B, ASTM D.5209-92, EN 29439.

<u>Criteria and pass levels</u>

- Biodegradability must be determined for the complete product/material or for each significant organic constituent. Significant means any organic constituent present in more than 1 % of dry weight of the material.
- The total proportion of organic constituents, not tested on biodegradability, may not exceed 5 %.
- The percentage of biodegradation shall be at least 90 % in total or 90 % of the maximum degradation of a suitable reference substance after a plateau has been reached for both test material and reference substance.
- The duration of the test after which the 90% limit must be reached is 2 years.

B.3. Ecotoxicity

Ecotoxicity or detrimental environmental effects shall be evaluated on a case by case situation depending on the available information and the rate of biodegradation in soil.

- Complete materials/products are approved if they fulfill the conditions of EN 13432 on ecotoxicity.
- Inorganic constituents are approved if they do not show any toxic effect in the OECD #208 test when tested at a concentration of 10 times a typical maximum dosage.
- Organic constituents should be evaluated on ecotoxicity after they have gone through an extensive biodegradation phase. A suitable test method is OECD #208.

V. Marking : (only applicable for the supply of an end product)

The certified products or, if not possible on the product, his packaging will have to bear the following indications:
* OK Biodegradable SOIL conformity mark, as well as a number to identify the holder of the mark
* For products, this logo shall appear at least once on every product or, if not possible, on the packaging (f.e. with liquids)
* Code of the manufacturer in order to be able to identify the batch.

VI. Possible extensions of the certification :

None

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[1] *Cosmetic changes – November 2005*

US006787613B2

(12) **United States Patent**
Bastioli et al.

(10) **Patent No.: US 6,787,613 B2**
(45) **Date of Patent: Sep. 7, 2004**

(54) **TERNARY MIXTURE OF BIODEGRADABLE POLYESTERS AND PRODUCTS OBTAINED THEREFROM**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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(65) **Prior Publication Data**

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Jan. 25, 2001 (IT) TO2001A0058

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(52) **U.S. Cl.** **525/411**; 525/444; 524/47
(58) **Field of Search** 525/411, 444; 524/47

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,883,199 A		3/1999	McCarthy et al.	
6,521,717 B1	*	2/2003	Itoh	525/444

FOREIGN PATENT DOCUMENTS

EP	0 327 505 A2	8/1989
EP	0 400 532 A1	12/1990
EP	0 965 615 A1	12/1990
EP	0 950 678 A1	10/1999
EP	0 980 894 A1	2/2000
EP	0 990 676 A1	4/2000
WO	90/10671	9/1990
WO	92/19680	11/1992
WO	99/8367	6/1999
WO	00/55236	9/2000

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(57) **ABSTRACT**

The invention relates to a mixture of biodegradable polyesters which includes an aromatic-aliphatic polyester (A), an aliphatic polyester (B) and a polyactic acid polymer (C) in which the concentration of A varies, with respect to (A+B) in the range between 40 and 70% by weight, and the concentration of C with respect to (A+B+C) is of between 6 and 30% by weight.

27 Claims, No Drawings

TERNARY MIXTURE OF BIODEGRADABLE POLYESTERS AND PRODUCTS OBTAINED THEREFROM

DESCRIPTION

The present invention relates to mixtures of biodegradable polyesters which include at least three polyesters in proportions whereby it is possible to provide biodegradable film with improved characteristics compared to the individual initial polyesters and demonstrating, in particular, properties of considerable strength, both longitudinally of and transverse the direction of the formation of the film, transparency and rigidity.

Film manufactured from such mixtures will prove particularly useful in food packaging, for mulching, for silage and in various other applications.

THE PRIOR ART

Conventional polymers such as low or high-density polyethylene are characterised not only by excellent flexibility and water resistance, but also by a good level of transparency and by excellent resistance to tearing. These polymers are used, for example, for sacks and bags, as packaging material and as film for agricultural mulching. However, their poor biodegradability has caused a problem of visual pollution which has steadily worsened over the past few decades.

Polymers such as L-polylactic, D,L-polylactic or D-polylactic acid and copolymers thereof are thermoplastic materials which are biodegradable, come from a renewable source, are transparent and have excellent resistance to mould and are thus well suited to packaging food products, contributing to preserving the organoleptic qualities thereof These materials, however, break down only slowly in the soil and, if composted, decompose only at high temperatures. However their main drawback is that the thin film obtained under normal conditions, by either the blown or cast methods, has a low tear resistance. In addition, these films are very stiff and thus unsuitable for mulching, for making food packaging bags, bin liners or other packaging films which do, however, require considerable strength.

The aliphatic polyesters, on the other hand, which are mainly constituted by monomers from renewable sources, based on diacids and diols, such as polymers of sebacic, brassylic or azelaic acid, for example, have the huge disadvantage of being highly anisotropic, with regard to resistance to both longitudinal and transverse tearing, and also show extremely poor resistance to longitudinal tearing. These characteristics also make film produced from these resins unsuitable for use in mulching, in food packaging or for bin liners and the like.

Polyhydroxy-acids, such as poly-ϵ-caprolactone, also have a typical tendency to a transverse orientation.

In order to maintain biodegradable characteristics conforming with the CEN 13432 method, biodegradable aliphatic-aromatic polymers, in particular polymers with the aromatic portion constituted by terephthalic acid and the aliphatic portion constituted by diacid diols, and/or hydroxy acids, with a C2–C20 aliphatic chain, either branched or not (possibly chain extended with isocyanates, anhydrides or epoxides) and, in particular, polymers based on terephthalic acid, adipic acid and butandiol, must contain quantities of terephthalic acid (as moles of the total acid) not exceeding 55% and preferably not exceeding 50%. Examples of this type of material include Ecoflex by BASF or Eastarbio by Eastman, which are strong but with extremely low moduli, of the order of 100 MPa or less.

Binary compounds of polylactic acid and aliphatic polyesters have formed the object of numerous patents. In particular, the Patent EP-0 980894 A1 (Mitsui Chemical) describes a significant improvement in tear resistance and in the balance of mechanical properties in film manufactured from mixtures of polylactic acid and polybutylenesuccinate, with the addition of a plasticizer.

However the films described are not transparent and have fairly low strengths, of the order of 120 g according to the JIS P8116 method. In addition, the presence of a plasticizer limits use of the film in contact with food products and, since it ages rather quickly, for use as an agricultural mulch.

The U.S. Pat. No. 5,883,199 describes binary compounds of polylactic acid and polyesters, with a polylactic acid content of between 10 and 90% and with the polyester forming either a continuous or co-continuous phase. The tear resistance of the compounds described here is very poor, however.

Object, characteristics and advantages of the invention

Starting from the need to find a biodegradable material which combined the two properties of transparency and tear resistance, it was a surprise to find that if the three different types of polyester described (lactic acid polymers, aliphatic polyester derived from diacids/diols and aromatic aliphatic polyester) were combined in specific ratios, there was a critical compositional range in which it was possible to achieve resistance to tearing in both directions, comparable to that of conventional plastics materials such as polyethylene, moduli of elasticity with values found between those of low and high-density polyethylene. It was found, even more surprisingly, that it was possible for the transparency of the ternary mixture of polyesters of the invention to be comparable to that of the individual component materials, even when drawn.

DESCRIPTION OF THE INVENTION

The invention relates to a mixture of biodegradable polyesters which includes:

(A) an aromatic-aliphatic polyester with a melting point of between 50 and 170° C. and preferably of between 80° and 120° C.;

(B) an aliphatic polyester with a molecular weight Mw greater than 40,000, and preferably>60,000 and a melting point of between 50° and 95° C., preferably of between 55° and 85° C., and even more preferably of between 57° and 80° C.;

(C) a polylactic acid polymer containing at least 75% of L-lactic or D-lactic acid or a combination thereof, with a molecular weight Mw greater than 30,000;

in which the concentration of A varies, with respect to (A+B), in the range between 40% and 70% by weight, and the concentration of C with respect to (A+B+C) is of between 6 and 30%, preferably of between 10 and 25% by weight.

More in particular, in the mixture of the invention:

(A), the aromatic-aliphatic polyester, is biodegradable according to the CEN13432 standard, it has (at T=23° and Relative Humidity=55%) a modulus which is less than 150 MPa, lengthens to breaking point by more than 500% for blown film with a thickness of 25–30 μm, tested within three days from production;

(B), the aliphatic polyester, preferably a diacid/diol type, has (at T=23° C. and Relative Humidity=55%) a modulus of elasticity of between 200 and 900 MPa and lengthens to breaking point by more than 200%, for blown film with a thickness of 25–30 μm, tested within three days of production;

(C), the polylactic acid polymer, has a modulus of more than 1,500 MPa.

The mixture of biodegradable polyesters of the invention is obtained in a process which is carried out in a two-screw or one-screw extruder at a temperature of between 100 and 200° C., either by a one-step method or a method involving separate steps of mixing and then film forming.

In the event of film forming being separate from the mixing operation, it is carried out by means of conventional machinery for polyethylene extrusion (high or low density), at a heat in the range of 100 to 200° C., preferably of 140 to 197° C. and more preferably of 185 to 195° C., with a blowing ratio normally in the range of 1.5–5 and a drawing ratio of between 3 and 100, preferably 3 and 25 and produces film with a thickness of between 5 and 50 μm.

Films of the invention, with a thickness of between 25–30 μm, show a tear resistance in both directions, according to the Elmendorf test, of between 15 and 100 N/mm, preferably of between 20 and 90 N/mm and even more preferably of between 25 and 80 N/mm, with a ratio of transverse to longitudinal Elmendorf values of between 3.5 and 0.4, and preferably of between 2.5 and 0.5. Such films have a modulus of between 150 and 800 MPa, preferably of between 250 and 750 MPa and prove biodegradable both in soil and when composted. Such films are also characterised by transparency, understood as transmittance at the entrance port measured on the HAZEGUARD SYSTEM XL-211 in the range between 85 and 90% when formed into a film at a head temperature of between 185° and 200° C.

During the mixing step, type (A) polymers are preferred with an MFI (ASTM standard D 1238-89) of between 1 and 10 dg/min, type (B) polymers are preferred with an MFI of between 1 and 10 dg/min and (C) type polymers are preferred with an MFI of between 2 and 30 dg/min.

The type (A) polymer family comprises polyesters obtained from the reaction of mixtures which contain (a^1) mixtures of from 35 to 95% moles of adipic acid, or derivatives in the form of esters or mixtures thereof, from 5 to 65% moles of terephthalic acid, or ester derivatives and mixtures thereof, and from 0 to 5% moles of a sulphur-containing compound, the sum of the percentages of the various components to be 100% (a^2) a compound with two hydroxyl functions selected from a group consisting of C2-C 6 alkandiols and C5–C10 cycloalkandiols, the molar ratio (a^1):(a^2) being in the interval between 0.4:1 and 1.5:1, it being possible for the polyester to have a molecular weight Mw of between 5,000 and 50,000, a viscosity of between 30 and 350 g/mole (measured in 50:50 w/w dichlorobenzene/phenol at a concentration of 0.5% of the weight of the polyester at 25° C.) and a melting point of between 50 and 170° C., and preferably of between 90 and 120° C. It is also possible to produce the polymer using a compound with at least three groups able to form ester bonds.

The polymer (B) is preferably constituted by dicarboxylic aliphatic acids from a renewable source such as azelaic acid, sebacic acid, brassylic acid or compounds thereof and aliphatic diols, and possibly also by hydroxy acids. Examples of diacids which can be used in combination with sebacic, azelaic or brassylic acid, or mixtures thereof, are succinic, oxalic, malonic, glutaric, adipic, pimelic, suberic, undecandioic or dodecandioic acids. Those polyesters are especially preferred which contain more than 50% by mole of azelaic, sebacic or brassylic acid, or mixtures thereof, out of the total quantity of acid, with those containing more than 70% by mole being even more strongly preferred and those containing more than 90% being yet more strongly preferred.

Specific glycols are ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, 1,2- and 1,3-propylene glycol, dipropylene glycol, 1,3-butandiol, 1,4-butandiol, 3-methyl-1,5-pentandiol, 1,6-hexandiol, 1,9-nonandiol, 1,11-undecandiol, 1,13-tridecandiol, neopentyl glycol, polytetramethylene glycol, 1,4-cyclohexane-dimethanol and cyclohexane-diol. These compounds can be used individually and in combination.

Typical hydroxy acids include glycolic acid, lactic acid, 3-hydroxybutyric, 4-hydroxybutyric, 3-hydroxyvaleric, 4-hydroxyvaleric and 6-hydroxycaproic acid, and also cyclic esters of hydroxycarboxylic acids such as glycolide, dimers of glycolic acid, epsilon-caprolactone and 6-hydroxycaproic acid. These compounds can be used individually or in combination. All the compounds mentioned above are combined so as to form polyesters with tensile mechanical characteristics of resistance to elongation>200% and preferably>300% with a modulus of between 200 and 900 MPa for blown film at least 25–30 μm thick, with a melting point of between 50° and 95° C., preferably of between 55° and 85° C. and more preferably of between 57° and 80° C.

The type B polymers also include polyamide polyesters in which the polyester portion is as described above and the polyamide portion can be caprolactan, an aliphatic diamine such as hexamethylenediamine or even an aminoacid. The B type polyesters may also contain a quantity of less than 5% moles of aromatic diacids. Polycarbonates also belong to the type B polymers.

Biodegradable polyesters forming part of the mixture of the invention can be polymerized by polycondensation or, as in the case of glycolide and the lactones, by the open-ring method, as known in the literature. The polyesters can also be branched polymers, with the introduction of polyfunctional monomers such as glycerine, epoxidized soya oil, trimethylolpropane and the like, or of polycarboxylic acids such as butantetracarboxylic acid. In addition, chain extenders such as difunctional, trifunctional or tetrafunctional anhydrides, for example maleic, trimellitic or pyromellitic anhydride, or expoxy, aliphatic or aromatic iso-cyanates group, can be added to A type polyesters.

The material can be regraded with iso-cyanates either in its molten state, at the end of the polymerization reaction or during extrusion, or in its solid state, as described in the Patent Application Novamont WO 99/28367. The three types, A, B and C, of polymer can also have chain extenders or cross-linking agents added to them during the mixing operation.

Higher concentrations of A than those of the range reported above for the mixture of the invention involve modulus characteristics which are too low, while lower concentrations of A bring a deterioration in laceration characteristics.

Higher concentrations of B than those of the range reported above for mixtures of the invention make the film more unbalanced and less strong, while lower concentrations mean that the film is insufficiently rigid.

Concentrations of C polymer below 6% have no significant effect on the balance of tearing properties in the two directions or on adjustment of the modulus.

Material obtained by mixing the three polymers A, B and C needs no plasticizers, which cause migration problems, especially in the case of food packaging. However, quantities of plasticizer of less than 5% of the polymers (B+C) can be added.

Various other additives can be incorporated into the mixture, such as anti-oxidants, UV stabilizers, heat and hydrolytic stabilizers, flame retardants, slow-release agents or organic or inorganic fillers such as natural fibres, anti-static agents, humectant agents, colourings or lubricants, for example.

In particular, in the production of film by the blown or cast methods, silica, calcium carbonate, talc, kaolin, kaolinite, zinc oxide and various wollastonites can be added, as can, generally speaking, inorganic lamellar substances functionalized or not with organic molecules, which are able to delamellate during the mixing stage with the polymeric mixture, or with one of the individual polymers thereof, so as to form nanocompounds with improved anti-blocking and barrier properties. The various inorganic substances can be used in combination or individually. The concentration of inorganic additives is generally of between 0.05 and 70%, preferably of between 0.5 and 50% and, even more preferably, of between 1 and 30%.

In the case of natural fibres and fillers, such as cellulose, sisal, ground nuts, corn husks, rice husks, soya and the like, preferred concentrations are of between 0.5 to 70%, preferably of between 1 and 50%. It is also possible to bulk out these materials with mixed inorganic and plant matter.

Aliphatic acid amides can be added to improve the film-forming characteristics of the material, such as oleamide, stearamide, erucamide, behenamide, N-oleylpalmitamide, N-stearylerucamide and other amides, salts of fatty acids such as aluminium, zinc or calcium stearate and the like. The quantity of these additives varies between 0.05 and 7 parts, and preferably between 0.1 and 5 parts of the polymeric mixture.

The mixture thus obtained can be turned into film by blowing or by extrusion with a flat head. The transparent film is strong, can be bonded perfectly and can be produced in thicknesses of up to 5 μm, either blown or cast. The film can be made into sacks and bags for carrying goods, film and bags for food packaging, stretchable, heat-shrinkable film, film for adhesive tape, for disposable nappy tapes and for decorative coloured tape. Some other main applications are for silage, for “breathable” bags for fruit and vegetables, bags for bread and other food products, film for covering packs of meats, cheese and other food items and yoghurt pots. The film can also be bi-orientated.

Film produced with compounds of the invention can also be used as a sealable component in composite materials with at least one layer of polylactic acid or another polyester, of starch which has or has not been destructured and blends thereof with synthetic or natural polymers, or in a compound material, layered with aluminium and other materials, or can be metallized under vacuum with aluminium, silica or other inorganic materials. The layers can be produced either by co-extrusion or by laminating or by extrusion coating, provided that one layer is paper, fabric or non-woven fabric and the other is a biodegradable material or another material which will not melt at the temperatures required to extrude the film.

The film can be used for agricultural mulching, possibly with the addition of UV stabilizers, either in the form of single layer film or co-extruded with a lower-modulus film, as in the case of starch-based materials, in order to improve UV resistance and barrier properties, and to slow down the speed of decomposition in the air and in the soil.

The material thus obtained can also be used to manufacture fibre for textiles and non-woven fabric, or for fishing nets. In addition, the non-woven fabric can be used for disposable diapers, sanitary protection and the like. The fibres can also be bonded to special types of paper as reinforcement.

The material can also be used successfully to manufacture sheets for either mono-extruded or co-extruded heat forming, with other polymeric layers such as polylactic acid, other polyesters or polyamides, starch-based materials or other materials, and then heat formed into trays for food packaging, agricultural containers and the like.

Other additives can also be added to the material, such as polyethylene or polypropylene waxes, PET and PTB, polystyrene, ethylene or propylene co-polymers with functional carboxyl groups, carboxylate, methacrylate, acrylate, or hydroxy groups, or it can be combined with such polymers in co-extrusion, co-injection or similar operations. The material can be used as a matrix in a blend with destructured starch, according to methods related in Patents EP-0 327505, EP-0 539541, EP-0 400532, EP-0 413798, EP-0 965615, in which it can bond with the starch.

It can be used as a coating film for biodegradable foam materials based on polyester, polyamides made from thermoplastic starch, complex starch or simply a blend of starch with other polymers, or with the material of the present invention.

The material can also be expanded, alone or mixed with starch or with other polymers for the manufacture of containers for fruit and vegetables, meat, cheese and other food products, of fast food containers or even of foam balls which can be moulded into foam elements for industrial packaging. It can be used as a foam in the place of polyethylene foam. It can also find application in the field of textiles and non-woven fabric for clothing, hygiene and industrial products, and also for fishing nets or nets for fruit and vegetables. The mixture of biodegradable polyesters of the invention will now be described by means of some non-limitative examples.

EXAMPLES

Example 1

Polymers constituting the mixture:

50% aliphatic-aromatic polyester (A): Ecoflex 0700 BASF;

40% aliphatic polyester (B): Polybutylensebacate made of sebacic acid and butandiol with a monobutylstanoic acid catalyst, as in example 1 of WO 00/55236;

10% polylactic acid polymer (C): 4040 Cargill with a 6% D-lactic content (MFI=4 dg/min).

The polymers were mixed in an OMC extruder:

Diameter 58 mm; L/D=36; rpm=160; heat profile 60-120-160×5-155×2

Absorption=80A. Delivery=40 kg/h

Film forming on Ghioldi machine:

Diameter=40 mm, L/D=30; rpm=45; die: diameter=100 mm; air gap=0.9 mm; land=12;

Delivery 13.5 kg/h

Heat profile: 110-130-145×2; filter temperature 190×2; head temperature=190×2

Film: width=400 mm; thickness 251 μm;

The film thus obtained was subjected to the Elmendorf tear-resistance test, carried out on a Lorentzen & Wettre pendulum. The test was carried out both transversely (Ecross) and longitudinally (Elong). The ratio between the two values (Ecross/Elong) shows the level of isotropy of the film in the two directions.

Transmittance values, determined both at the source port (Tsource)and at the entrance port (Tentr), were carried out with an XL-211 HAZEGUARD SYSTEM measurer. The modulus of elasticity (E) values, breakage load (σ) and breakage elongation (ε) were determined in accordance with ASTM D 882-91 with an INSTRON 4502 instrument.

The results of the tests are reported in Table 1

Examples 2–10

While maintaining the conditions of mixture extrusion and film forming related in example 1, the percentages of the polymers constituting the mixture were varied. The results of the tests on the film thus produced are given in Table 1. In Example 10, polybutylensebacate was replaced with poly-ε-caprolactone.

The results thus obtained demonstrated how the ranges of concentration of the polymers in the mixture are crucial to the simultaneous achievement of considerable mechanical and transparency characteristics of the film, which prove so useful in countless practical applications.

Examples for Comparison

While maintaining the conditions of mixture extrusion and of film forming related in Example 1, binary mixtures were tested, which each time contained only two of the polymers constituting the mixture of the invention. The results of the tests on film thus produced are given in Table 2. In Example 3c, polybutylensebacate was replaced with poly-ε-caprolactone.

TABLE 1

Es.	A %	B %	C %	A/ A + B	C/ A + B + C	E_{cross} N/^{s}mm	E_{long} N/mm	E_{cross}/ E_{long}	T_{source} %	T_{entr} %	E (Mpa)	σ (MPa)	ε (%)
1.	60	30	10	66.6	10	47.8	81	0.59	72.7	89	527	36	458
2.	50	40	10	55.5	10	44.9	52.4	0.85	65.2	89.4	549	34	446
3.	45	45	10	50.0	10	57.5	20.2	2.84	64.1	89.6	511	36	490
4.	40	50	10	44.4	10	49.3	33.1	1.49	63.5	89.9	576	35	450
5.	50	30	20	62.5	20	32.5	37.4	0.86	61.8	87.0	776	32	354
6.	40	40	20	50.0	20	37.8	42.9	0.88	45.5	87.8	757	31	353
7.	20	40	40	33.3	40	7.4	9.1	0.81	41.2	88.5	1321	37	319
8.	50	45	5	52.6	5	80.2	17.8	4.5	—	—	328	32	609
9.	50	48	2	51.0	2	134	12	11.16	—	—	242	31	674
10	50	40	10	55.5	10	13.9	10.7	1.30	75.0	89.0	567	30	576

TABLE 2

Es.	A %	B %	C %	E_{cross} N/mm	E_{long} N/mm	E_{cross}/ E_{long}	T_{source} %	T_{entr} %	E (Mpa)	σ (MPa)	ε (%)
1a	0	50	50	7.1	6.4	1.1	68.5	93	2007	35	60
1b	0	60	40	10.7	5.1	2.09	38.5	90.4	1464	36.5	362
1c	0	40	60	7.8	8.6	0.90	73	92	2018	34	69
2a	50	0	50	8.1	7.2	1.1	57.3	85.6	1416	39	394
2b	60	0	40	12.8	7.8	1.64	36.5	82.1	1122	39	361
3a	60	40	0	194	6.98	27.8	65	87	215	42	499
3b	50	50	0	219	6.14	35.7	75	93	245	41	452
3c	50	50	0	246	8	30.8	80	90	—	—	—
3d	30	70	0	84.8	7	12.1	—	—	281	42	426

What is claimed is:

1. A mixture of biodegradable polyesters which includes:

A. an aromatic-aliphatic polyester with a melting point of between 50° and 170° C.;

B. an aliphatic polyester with a molecular weight Mw greater than 60,000 and a melting point between 50° and 95° C.;

C. A polylactic acid polymer which contains at least 75% of L-lactic or D-lactic acid, or combinations thereof, with a molecular weight Mw greater than 30,000, in which the concentration of A varies with respect to (A+B) in the range of between 40 and 70% by weight, and the concentration of C with respect to (A+B+C) is of between 6 and 30%.

2. A mixture of biodegradable polyesters according claim **1** in which the concentration of C with respect to (A+B+C) is of between 10 and 25% by weight.

3. A mixture of biodegradable polyesters according to claim **1**, in which the aliphatic polyester (B) is a diacid/diol obtained from an aliphatic diacid from renewable source and makes up more than 50% in moles of the total diacid content.

4. A mixture of biodegradable polyesters according to claim **3** in which the dicarboxylic aliphatic diacid is selected from azelaic, sebacic or brassylic acid and makes up more than 50% in moles of the total diacid content.

5. A mixture of biodegradable polyesters according to claim **1** in which the aliphatic polyester (B) is poly-epsilon-caprolactone or co-polymers thereof.

6. A mixture of biodegradable polyesters according to any one of claims **1–5**, in which the modulus of the aromatic-aliphatic polyester (A) is less than 150 MPa and its elongation to breaking is greater than 500% for film with a thickness of between 25–30 μm produced by the blown method.

7. A mixture of biodegradable polyesters according to any one of claims **1–5** in which the modulus of elasticity of the aliphatic polyester (B) is of between 200 and 900 MPa and its elongation to breaking is greater than 200%, for film with a thickness of between 25–30 μm produced by the blown method.

8. A mixture of biodegradable polyesters according to claim **7**, in which the elongation to breaking of the aliphatic polyester (B) is greater than 300%.

9. A mixture of biodegradable polyesters according to any one of claims **1–5** in which the modulus of the polylactic acid polymer (C) is greater than 1,500 MPa.

10. A mixture of biodegradable polyesters according to claim **1**, in which:

the aromatic-aliphatic polyester (A) has a modulus of less than 150 MPa, elongation to breaking of more than

500% for film with a thickness of 25–30 μm, produced by the blown method;

the aliphatic polyester (B) has a modulus of elasticity between 200 and 900 MPa, elongation to breaking of more than 200%, for film with a thickness of 25–30 μm, produced by bubble forming; and

the polylactic acid polymer (C) has a modulus greater than 1,500 MPa.

11. A mixture of biodegradable polyesters according to claim **10**, in which the elongation to breaking of the aliphatic polyester (B) is greater than 300%.

12. A mixture of biodegradable polyesters according to any one of claims **1–5**, and **11** which the aromatic-aliphatic polyester is biodegradable according to standard CEN13432.

13. A mixture of biodegradable polyesters according to any one of claims **1–5**, and **11** in which the melting point of the aromatic-aliphatic polyester (A) is of between 80° and 120° C.

14. A mixture of biodegradable polyesters according to any one of claims **1–5** and **11** which the melting point of the aliphatic polyester (B) is of between 55 and 85° C.

15. A film produced from mixtures of biodegradable polyesters according to any one of claims **1–5**, **10** and **11**.

16. A film according to claim **15**, characterized by tear resistance in both directions, according to the Elmendorf test, of between 15 and 100 N/mm.

17. A film according to claim **16**, characterized in that the ratio of transverse to longitudinal tear resistance, according to the Elmendorf test, is of between 3.5 and 0.4.

18. A film according to claim **15**, characterized by tear resistance in both directions, according to the Elmendorf test, of between 20 and 90 N/mm.

19. A film according to claim **15**, characterized by tear resistance in both directions according to the Elmendorf test, of between 25 and 80 N/mm.

20. A film according to claim **19** in the form of food packaging, for containing organic residue and for agricultural mulching.

21. A film according to claim **15**, characterized in that the modulus value is of between 150 and 800 MPa.

22. A film according to claim **15**, characterized in that the modulus value is of between 250 and 750 MPa.

23. Compact sheet manufactured with a mixture according to any one of claim **1–5**, **10** and **11** for food containers, containers for seedlings and industrial containers in general.

24. Foam sheet manufactured with a mixture according to any one of claims **1–5**, **10** and **11** for food and other containers and for industrial packaging.

25. Fibers manufactured with a mixture according to anyone of claims **1–5**, **10** and **11** for textiles and non-woven fabrics used in the hygiene, fashion and industrial sectors.

26. A coating material comprising a mixture according to any one of claims **1–5**, **10** and **11**, for application to paper, textiles, non-woven fabrics or other layers of compact or expanded biodegradable material.

27. A mixture of biodegradable polyesters according to any one of claims **1–5**, **5**, **10** and **11** in combination with destructed starch, natural starch or modified starch, wherein the starch is in a complex or not complex dispersed phase.

* * * * *

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(54) **TERNARY MIXTURES OF BIODEGRADABLE POLYESTERS AND PRODUCTS MANUFACTURED FROM THEM**

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(57) **ABSTRACT**

The invention relates to a mixture of biodegradable polyesters which includes an aromatic-aliphatic polyester (A), an aliphatic polyester (B) and a polylactic acid polymer (C) in which the concentration of A varies, with respect to (A+B) in the range between 40 and 70% by weight, and the concentration of C with respect of (A+B+C) is of between 6 and 30% by weight.

34 Claims, No Drawings

TERNARY MIXTURES OF BIODEGRADABLE POLYESTERS AND PRODUCTS MANUFACTURED FROM THEM

The present invention relates to mixtures of biodegradable polyesters which include at least three polyesters in proportions whereby it is possible to provide biodegradable film with improved characteristics compared to the individual initial polyesters and demonstrating, in particular, properties of considerable strength, both longitudinally of and transverse the direction of the formation of the film, transparency and rigidity.

Film manufactured from such mixtures will prove particularly useful in food packaging, for mulching, for silage and in various other applications.

THE PRIOR ART

Conventional polymers such as low or high-density polyethylene are characterised not only by excellent flexibility and water resistance, but also by a good level of transparency and by excellent resistance to tearing. These polymers are used, for example, for sacks and bags, as packaging material and as film for agricultural mulching. However, their poor biodegradability has caused a problem of visual pollution which has steadily worsened over the past few decades.

Polymers such as L-polylactic, D,L-polylactic or D-polylactic acid and copolymers thereof are thermoplastic materials which are biodegradable, come from a renewable source, are transparent and have excellent resistance to mould and are thus well suited to packaging food products, contributing to preserving the organoleptic qualities thereof. These materials, however, break down only slowly in the soil and, if composted, decompose only at high temperatures. However their main drawback is that the thin film obtained under normal conditions, by either the blown or cast methods, has a low tear resistance. In addition, these films are very stiff and thus unsuitable for mulching, for making food packaging bags, bin liners or other packaging films which do, however, require considerable strength.

The aliphatic polyesters, on the other hand, which are mainly constituted by monomers from renewable sources, based on diacids and diols, such as polymers of sebacic, brassylic or azelaic acid, for example, have the huge disadvantage of being highly anisotropic, with regard to resistance to both longitudinal and transverse tearing, and also show extremely poor resistance to longitudinal tearing. These characteristics also make film produced from these resins unsuitable for use in mulching, in food packaging or for bin liners and the like.

Polyhydroxy-acids, such as poly-ϵ-caprolactone, also have a typical tendency to a transverse orientation.

In order to maintain biodegradable characteristics conforming with the CEN 13432 method, biodegradable aliphatic-aromatic polymers, in particular polymers with the aromatic portion constituted by terephthalic acid and the aliphatic portion constituted by diacid diols, and/or hydroxy acids, with a C2–C20 aliphatic chain, either branched or not (possibly chain extended with isocyanates, anhydrides or epoxides) and, in particular, polymers based on terephthalic acid, adipic acid and butandiol, must contain quantities of terephthalic acid (as moles of the total acid) not exceeding 55% and preferably not exceeding 50%. Examples of this type of material include Ecoflex by BASF or Eastarbio by Eastman, which are strong but with extremely low moduli, of the order of 100 MPa or less.

Binary compounds of polylactic acid and aliphatic polyesters have formed the object of numerous patents. In particular, the Patent EP-0 980894 A1 (Mitsui Chemical) describes a significant improvement in tear resistance and in the balance of mechanical properties in film manufactured from mixtures of polylactic acid and polybutylenesuccinate, with the addition of a plasticizer.

However the films described are not transparent and have fairly low strengths, of the order of 120 g according to the JIS P8116 method. In addition, the presence of a plasticizer limits use of the film in contact with food products and, since it ages rather quickly, for use as an agricultural mulch.

The U.S. Pat. No. 5,883,199 describes binary compounds of polylactic acid and polyesters, with a polylactic acid content of between 10 and 90% and with the polyester forming either a continuous or co-continuous phase. The tear resistance of the compounds described here is very poor, however.

OBJECT, CHARACTERISTICS AND ADVANTAGES OF THE INVENTION

Starting from the need to find a biodegradable material which combined the two properties of transparency and tear resistance, it was a surprise to find that if the three different types of polyester described (lactic acid polymers, aliphatic polyester derived from diacids/diols and aromatic aliphatic polyester) were combined in specific ratios, there was a critical compositional range in which it was possible to achieve resistance to tearing in both directions, comparable to that of conventional plastics materials such as polyethylene, moduli of elasticity with values found between those of low and high-density polyethylene. It was found, even more surprisingly, that it was possible for the transparency of the ternary mixture of polyesters of the invention to be comparable to that of the individual component materials, even when drawn.

DESCRIPTION OF THE INVENTION

The invention relates to a mixture of biodegradable polyesters which includes:

(A) an aromatic-aliphatic polyester with a melting point of between 50 and 170° C. and preferably of between 80° and 120° C.;

(B) an aliphatic polyester with a molecular weight Mw greater than 40,000, and preferably >60,000 and a melting point of between 40° and 170° C., preferably of between 50° and 145° C., and even more preferably of between 55° and 130° C.;

(C) a polylactic acid polymer containing at least 75% of L-lactic or D-lactic acid or a combination thereof, with a molecular weight Mw greater than 30,000;

in which the concentration of A varies, with respect to (A+B), in the range between 40% and 70% by weight, and the concentration of C with respect to (A+B+C) is of between 5 and 30%, preferably of between 5 and 20% by weight.

More in particular, in the mixture of the invention:

(A), the aromatic-aliphatic polyester, is biodegradable according to the CEN13432 standard, it has (at T=23° and Relative Humidity=55%) a modulus which is less than 150 MPa, lengthens to breaking point by more than 500% for blown film with a thickness of 25–30 μm, tested within three days from production;

(B), the aliphatic polyester, preferably a diacid/diol type and/or a polyhydroxyacid type, has (at T=23° C. and Relative Humidity=55%) a modulus of elasticity of between 200 and 1500 MPa and lengthens to breaking point by more than 20%, preferably more than 100%, for blown film with a thickness of 25–30 μm, tested within three days of production;

(C), the polylactic acid polymer, has a modulus of more than 1,500 MPa.

The mixture of biodegradable polyesters of the invention is obtained in a process which is carried out in a two-screw or one-screw extruder at a temperature of between 100 and 200° C., either by a one-step method or a method involving separate steps of mixing and then film forming or injection molding and so on.

In the event of film forming being separate from the mixing operation, it is carried out by means of conventional machinery for polyethylene extrusion (high or low density), at a heat in the range of 100° to 200° C., preferably of 140 to 197 and more preferably of 185 to 195° C., with a blowing ratio normally in the range of 1.5–5 and a drawing ratio of between 3 and 100, preferably 3 and 25 and produces film with a thickness of between 5 and 50 μm.

Films of the invention, with a thickness of between 25–30 μm, show a tear resistance in both directions, according to the Elmendorf test, of between 10 and 100 N/mm, preferably of between 15 and 90 N/mm and even more preferably of between 20 and 80N/mm, with a ratio of transverse to longitudinal Elmendorf values of between 4.5 and 0.4, and preferably of between 3 and 0.5. Such films have a modulus of between 150 and 1200 MPa, preferably of between 250 and 1000 MPa and prove biodegradable both in soil and when composted. Such films are also characterised by transparency, understood as transmittance at the entrance port measured on the HAZEGUARD SYSTEM XL-211 in the range between 85 and 90% when formed into a film at a head temperature of between 185° and 200° C.

During the mixing step, type (A) polymers are preferred with an MFI (ASTM standard D 1238-89) of between 1 and 10 dg/min, type (B) polymers are preferred with an MFI of between 1 and 10 dg/min and (C) type polymers are preferred with an MFI of between 2 and 30 dg/min.

The type (A) polymer family comprises polyesters obtained from the reaction of mixtures which contain (a^1) mixtures of from 35 to 95% moles of adipic acid, or derivatives in the form of esters or mixtures thereof, from 5 to 65% moles of terephthalic acid, or ester derivatives and mixtures thereof, and from 0 to 5% moles of a sulphur-containing compound, the sum of the percentages of the various components to be 100% (a^2) a compound with two hydroxyl functions selected from a group consisting of C2–C6 alkandiols and C5–C10 cycloalkandiols, the molar ratio (a^1):(a^2) being in the interval between 0.4:1 and 1.5:1, it being possible for the polyester to have a molecular weight Mw of between 5,000 and 50,000, a viscosity of between 30 and 350 g/mole (measured in 50:50 w/w dichlorobenzene/phenol at a concentration of 0.5% of the weight of the polyester at 25° C.) and a melting point of between 50 and 170° C., and preferably of between 90 and 120° C. It is also possible to produce the polymer using a compound with at least three groups able to form ester bonds.

The polymer (B) is preferably constituted by dicarboxylic aliphatic acids and aliphatic diols, and possibly also by hydroxy acids. Preferably the polymer (B) is also constituted by hydroxyacids. Examples of diacids which can be used are succinic, oxalic, malonic, glutaric, adipic, pimelic, suberic, undecandioic, dodecandioic, sebacic, azelaic or brassylic acids. Particularly preferred are sebacic, azelaic or brassylic acid, or mixtures thereof.

Specific glycols are ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, 1,2- and 1,3-propylene glycol, dipropylene glycol, 1,3-butandiol, 1,4-butandiol, 3-methyl-1,5-pentandiol, 1,6-hexandiol, 1,9-nonandiol, 1,11-undecandiol, 1,13-tridecandiol, neopentyl glycol, polytetramethylene glycol, 1,4-cyclohexane-dimethanol and cyclohexane-diol. These compounds can be used individually and in combination.

Typical hydroxy acids include C_2–C_{22} hydroxy acids such as, for example, glycolic acid, lactic acid, 3-hydroxybutyric, 4-hydroxybutyric, 3-hydroxyvaleric, 4-hydroxyvaleric and 6-hydroxycaproic acid and so on, and also cyclic esters of hydroxycarboxylic acids such as glycolide, dimers of glycolic acid, epsilon-caprolactone and 6-hydroxycaproic acid. These compounds can be used individually or in combination.

All the compounds mentioned above are combined so as to form polyesters with tensile mechanical characteristics of resistance to elongation >25% and preferably >100% with a modulus of between 200 and 1500 MPa for blown film at least 25–30 μm thick, with a melting point of between 40° and 170° C., preferably of between 50° and 145° C. and more preferably of between 55° and 130° C.

Particularly preferred are polyesters containing more than 50%, and preferably more than 70%, moles with respect to the total acid content of azelaic acid, sebacic acid, brassilic acid or mixture thereof. Also preferred are polyhydroxyacids obtained by process of synthesis from bacteria or plants or other biological processes such as copolymers of hydroxybutirrate and C_5–C_{20} hydroxyacids.

The type B polymers also include polyamide polyesters in which the polyester portion is as described above and the polyamide portion can be caprolactam, an aliphatic diamine such as hexamethylenediamine or even an aminoacid. The B type polyesters may also contain a quantity of less than 5% moles of aromatic diacids. Polycarbonates also belong to the type B polymers.

Biodegradable polyesters forming part of the mixture of the invention can be polymerized by polycondensation or, as in the case of glycolide and the lactones, by the open-ring method, as known in the literature. They can be synthetized also by microorganisms or plants. The polyesters can also be branched polymers, with the introduction of polyfunctional monomers such as glycerine, epoxidized soya oil, trimethylolpropane and the like, or of polycarboxylic acids such as butantetracarboxylic acid. In addition, chain extenders such as difunctional, trifunctional or tetrafunctional anhydrides, for example maleic, trimellitic or pyromellitic anhydride, or expoxy, aliphatic or aromatic iso-cyanates group, can be added to A type polyesters.

The material can be regraded with iso-cyanates either in its molten state, at the end of the polymerization reaction or during extrusion, or in its solid state, as described in the Patent Application Novamont WO 99/28367. The three types, A, B and C, of polymer can also have chain extenders or cross-linking agents added to them during the mixing operation.

Higher concentrations of A than those of the range reported above for the mixture of the invention involve modulus characteristics which are too low, while lower concentrations of A bring a deterioration in laceration characteristics.

Higher concentrations of B than those of the range reported above for mixtures of the invention make the film more unbalanced and less strong, while lower concentrations mean that the film is insufficiently rigid.

Concentrations of C polymer below 5% have no significant effect on the balance of tearing properties in the two directions or on adjustment of the modulus.

Material obtained by mixing the three polymers A, B and C needs no plasticizers, which cause migration problems, especially in the case of food packaging. However, quantities of plasticizer of less than 5% of the polymers (B+C) can be added.

Various other additives can be incorporated into the mixture, such as anti-oxidants, UV stabilizers, heat and hydrolytic stabilizers, flame retardants, slow-release agents or organic or inorganic fillers such as natural fibres, antistatic agents, humectant agents, colourings or lubricants, for example.

In particular, in the production of film by the blown or cast methods, silica, calcium carbonate, talc, kaolin, kaolinite, zinc oxide and various wollastonites can be added, as can, generally speaking, inorganic lamellar substances functionalized or not with organic molecules, which are able to delamellate during the mixing stage with the polymeric mixture, or with one of the individual polymers thereof, so as to form nanocompounds with improved anti-blocking and barrier properties. The various inorganic substances can be used in combination or individually. The concentration of inorganic additives is generally of between 0.05 and 70%, preferably of between 0.5 and 50% and, even more preferably, of between 1 and 30%. Particularly preferred are wollastonites and similar organophile substances.

In the case of natural fibres and fillers, such as cellulose, sisal, ground nuts, corn husks, rice husks, soya and the like, preferred concentrations are of between 0.5 to 70%, preferably of between 1 and 50%. It is also possible to bulk out these materials with mixed inorganic and plant matter.

Aliphatic acid amides can be added to improve the film-forming characteristics of the material, such as oleamide, stearamide, erucamide, behenamide, N-oleylpalmitamide, N-stearylerucamide and other amides, salts of fatty acids such as aluminium, zinc or calcium stearate and the like. The quantity of these additives varies between 0.05 and 7 parts, and preferably between 0.1 and 5 parts of the polymeric mixture.

The mixture thus obtained can be turned into film by blowing or by extrusion with a flat head. The transparent film is strong, can be bonded perfectly and can be produced in thicknesses of up to 5 μm, either blown or cast. The film can be made into sacks and bags for carrying goods, film and bags for food packaging, stretchable, heat-shrinkable film, film for adhesive tape, for disposable nappy tapes and for. decorative coloured tape. Some other main applications are for silage, for “breathable” bags for fruit and vegetables, bags for bread and other food products, film for covering packs of meats, cheese and other food items and yoghurt pots. The film can also be bi-orientated.

Film produced with compounds of the invention can also be used as a sealable component in composite materials with at least one layer of polylactic acid or another polyester, of starch which has or has not been destructured and blends thereof with synthetic or natural polymers, or in a compound material, layered with aluminium and other materials, or can be metallized under vacuum with aluminium, silica or other inorganic materials. The layers can be produced either by co-extrusion or by laminating or by extrusion coating, provided that one layer is paper, fabric or non-woven fabric and the other is a biodegradable material or another material which will not melt at the temperatures required to extrude the film.

The film can be used for agricultural mulching, possibly with the addition of UV stabilizers, either in the form of single layer film or co-extruded with a lower-modulus film, as in the case of starch-based materials, in order to improve UV resistance and barrier properties, and to slow down the speed of decomposition in the air and in the soil.

The material thus obtained can also be used to manufacture fibre for textiles and non-woven fabric, or for fishing nets.

In addition, the non-woven fabric can be used for disposable diapers, sanitary protection and the like. The fibres can also be bonded to special types of paper as reinforcement.

The material can also be used successfully to manufacture sheets for either mono-extruded or co-extruded heat forming, with other polymeric layers such as polylactic acid, other polyesters or polyamides, starch-based materials or other materials, and then heat formed into trays for food packaging, agricultural containers and the like.

Other additives can also be added to the material, such as polyethylene or polypropylene waxes, PET and PTB, polystyrene, ethylene or propylene co-polymers with functional carboxyl groups, carboxylate, methacrylate, acrylate, or hydroxy groups, or it can be combined with such polymers in co-extrusion, co-injection or similar operations. The material can be used as a matrix in a blend with destructured starch, according to methods related in Patents EP-0 327505, EP-0 539541, EP-0 400532, EP-0 413798, EP-0 965615, in which it can bond with the starch.

It can be used as a coating film for biodegradable foam materials based on polyester, polyamides made from thermoplastic starch, complex starch or simply a blend of starch with other polymers, or with the material of the present invention.

The material can also be expanded, alone or mixed with starch or with other polymers for the manufacture of containers for fruit and vegetables, meat, cheese and other food products, of fast food containers or even of foam balls which can be moulded into foam elements for industrial packaging. It can be used as a foam in the place of polyethylene foam. It can be used in the injection molding field for example in order to produce cutlery, food containers, containers for agriculture and industry, pharmaceutical containers and so on.

It can also find application in the field of textiles and non-woven fabric for clothing, hygiene and industrial products, and also for fishing nets or nets for fruit and vegetables.

The mixture of biodegradable polyesters of the invention will now be described by means of some non-limitative examples.

EXAMPLES

Example 1

Polymers constituting the mixture:

50% aliphatic-aromatic polyester (A): Ecoflex 0700 BASF;

40% aliphatic polyester (B): Polybutylensebacate made of sebacic acid and butandiol with a monobutylstanoic acid catalyst, as in example 1 of WO 00/55236;

10% polylactic acid polymer (C): 4040 Cargill with a 6% D-lactic content (MFI=4 dg/min).

The polymers were mixed in an OMC extruder:

Diameter 58 mm; L/D=36; rpm=160; heat profile 60-120-160×5-155×2

Absorption=80A. Delivery=40 kg/h

Film forming on Ghioldi machine:

Diameter=40 mm, L/D=30; rpm=45; die: diameter=100 mm; air gap=0.9 mm; land=12; Delivery 13.5 kg/h

Heat profile: 110-130-145×2; filter temperature 190×2; head temperature=190×2

Film: width=400 mm; thickness 25 μm;

The film thus obtained was subjected to the Elmendorf tear-resistance test, carried out on a Lorentzen & Wettre pendulum. The test was carried out both transversely (Ecross) and longitudinally (Elong). The ratio between the two values (Ecross/Elong) shows the level of isotropy of the film in the two directions.

Transmittance values were determined both at the source port (Tsource) And at the entrance port (Tentr), was carried out with an XL-211 HAZEGUARD SYSTEM measurer.

The modulus of elasticity (E) values, breakage load (σ) and breakage elongation (ϵ) were determined in accordance with ASTM D 882-91 with an INSTRON-4502 instrument.

The results of the tests are reported in Table 1

Examples 2–11

While maintaining the conditions of mixture extrusion and film forming related in example 1, the percentages of the polymers constituting the mixture were varied. The results of the tests on the film thus produced are given in Table 1. In Example 10, polybutylensebacate was replaced with poly-ϵ-caprolactone. In example 11 polybutylensebacate was replaced with polybutylensuccinate (Bionolle 1903, Showa Denko).

The results thus obtained demonstrated how the ranges of concentration of the polymers in the mixture are crucial to the simultaneous achievement of considerable mechanical and transparency characteristics of the film, which prove so useful in countless practical applications.

Examples for Comparison

While maintaining the conditions of mixture extrusion and of film forming related in Example 1, binary mixtures were tested, which each time contained only two of the polymers constituting the mixture of the invention. The results of the tests on film thus produced are given in Table 2. In Example 3c, polybutylensebacate was replaced with poly-ϵ-caprolactone.

Comparison of the data displayed in the two tables is clear evidence of the considerable improvement in the mechanical properties of film manufactured with polymeric mixtures of the invention.

TABLE 1

Es	A %	B %	C %	A/ A + B	C/ A + B + C	E_{cross} N/mm	E_{long} N/mm	E_{cross}/ E_{long}	T_{source} %	T_{entr} %	E (Mpa)	σ (MPa)	ϵ (%)
1	60	30	10	66.6	10	47.8	81	0.59	72.7	89	527	36	458
2	50	40	10	55.5	10	44.9	52.4	0.85	65.2	89.4	549	34	446
3	45	45	10	50.0	10	57.5	20.2	2.84	64.1	89.6	511	36	490
4	40	50	10	44.4	10	49.3	33.1	1.49	63.5	89.9	576	35	450
5	50	30	20	62.5	20	32.5	37.4	0.86	61.8	87.0	776	32	354
6	40	40	20	50.0	20	37.8	42.9	0.88	45.5	87.8	757	31	353
7	20	40	40	33.3	40	7.4	9.1	0.81	41.2	88.5	1321	37	319
8	50	45	5	52.6	5	80.2	17.8	4.5	—	—	328	32	609
9	50	48	2	51.0	2	134	12	11.16	—	—	242	31	674
10	50	40	10	55.5	10	13.9	10.7	1.30	75.0	89.0	567	30	576
11	50	40	10	55.5	10	14.2	13.5	1.02	60.1	88.1	502	37	589

TABLE 2

Es.	A %	B %	C %	E_{cross} N/mm	E_{long} N/mm	E_{cross}/ long	T_{source} %	T_{entr} %	E (Mpa)	σ (MPa)	ϵ (%)
1a	0	50	50	7.1	6.4	1.1	68.5	93	2007	35	60
1b	0	60	40	10.7	5.1	2.09	38.5	90.4	1464	36.5	362
1c	0	40	60	7.8	8.6	0.90	73	92	2018	34	69
2a	50	0	50	8.1	7.2	1.1	57.3	85.6	1416	39	394
2b	60	0	40	12.8	7.8	1.64	36.5	82.1	1122	39	361
3a	60	40	0	194	6.98	27.8	65	87	215	42	499
3b	50	50	0	219	6.14	35.7	75	93	245	41	452
3c	50	50	0	246	8	30.8	80	90	—	—	—
3d	30	70	0	84.8	7	12.1	—	—	281	42	426

The invention claimed is:

1. A mixture of biodegradable polyesters which includes:

(A) an aromatic-aliphatic polyester wit a melting point of between 50° and 170° C.;

(B) an aliphatic polyester with a molecular weight M_w greater than 40,000 and a melting point of between 40° and 170° C. ;

(C) a polylactic acid polymer which contains at least 75% of L-lactic or D-lactic acid, or combinations thereof, with a molecular weight M_w greater than 30,000, in which the concentration of A varies with respect to (A+B) in the range of between 40 and 70% by weight and the concentration of C with respect to (A+B+C) is of between 5 and 30%.

2. A mixture of biodegradable polyesters according to claim **1**, in which the modulus of the aromatic-aliphatic polyester (A) is less than 150 MPa and its elongation to breaking is greater than 500% for film with a thickness of between 25–30 μm produced by the blown method.

3. A mixture of biodegradable polyesters according to claim **1**, in which the modulus of elasticity of the aliphatic polyester (B) is of between 200 and 1500 MPa and its elongation to breaking is greater than 25% for film with a thickness of between 25–30 μm, produced by the blown method.

4. A mixture of biodegradable polyesters according to claim **1**, in which the modulus of the polylactic acid polymer (C) is greater than 1,500 MPa.

5. A mixture of biodegradable polyesters according to claim **1**, in which:

the aromatic-aliphatic polyester (A) has a modulus of less than 150 MPa, elongation to breaking of more than 500% for film with a thickness of 25–30 μm, produced by the blown method;

the aliphatie polyester polyester (B) has a modulus of elasticity of between 200 and 1500 MPa, elongation to breaking of more than 25% for film with a thickness of 25–30 m, produced by bubble forming; the polylactic acid polymer (C) has a modulus greater than 1,500 MPa.

6. A mixture of biodegradable polyesters according to claim **1** in which the aromatic-aliphatic polyester is biodegradable according to standard CEN 13432.

7. A mixture of biodegradable polyesters according to claim **1** in which the melting point of the aromatic-aliphatic polyester (A) is of between 50° and 170° C.

8. A mixture of biodegradable polyesters according to claim **1** in which the molecular weight of the aliphatic polyester (B) is M_w>40,000, and its melting point is of between 40° and 170° C.

9. Mixture of biodegradable polyesters according to claim **1** in which the polyester (B) is of the diacid/diol type.

10. Mixture of biodegradable polyesters according to claim **1** wherein the polyester (B) is a polyhydroxyacid.

11. Mixture of biodegradable polyesters according to claim **10** wherein the polyester (B) is polycapralacton and/or its copolymers.

12. Mixture of biodegradable polyesters according to claim **10** wherein the polyester (B) is a polyhydroxyalcanoate.

13. Mixture of biodegradable polyesters according to claim **9** wherein the aliphatic polyester (B) contains as diacid, azelaic acid, sebacic acid, brassilic acid, or mixtures thereof in a concentration, with respect to the total acid content, higher than 50 % moles.

14. Mixtures of biodegradable polyesters according to claim **1** together with destructurized starch, native starch or modified starch wherein the starch, either complexed or not complexed, is present in a dispersed phase.

15. Film produced from mixtures of biodegradable polyesters according to claim **1**.

16. Film according to claim **15**, characterized by tear resistance in both directions, according to the Elmendorf test, of between 10 and 100 N/mm.

17. A film according to claim **16**, characterized in that the ratio of transverse to longitudinal tear resistance, according to the Elmendorf test, is between 4.5 and 0.4.

18. Film according to claim **15** characterized in that the modulus value is of between 150 and 1200 MPa.

19. Food packaging, or packaging for containing organic residue or for agricultural mulching comprising the film according to claim **15**.

20. Compact sheet manufactured with mixtures according to claim **1** for food containers, containers for seedlings and industrial containers in general.

21. Foam sheet manufactured with mixtures according to claim **1** for food or other containers or for industrial packaging.

22. Fibres manufactured with mixtures according to claim **1** for textiles and non-woven fabrics used in the hygiene, fashion and industrial sectors.

23. A coating material manufactured with mixtures according to claim **1** for application to paper, textiles, non-woven fabrics or other layers of compact or expanded biodegradable material.

24. A mixture of biodegradable polyesters according to claim **1** wherein the concentration of C with respect to (A+B+C) is between 5 and 20% by weight.

25. A mixture of biodegradable polyesters according to claim **1** wherein the elongation to breaking of the aliphatic polyester (B) is >100%.

26. A mixture of biodegradable polyesters according to claim **5** wherein the elongation to breaking of the aliphatic polyester (B) is >100%.

27. A mixture of biodegradable polyesters according to claim **1** in which the melting point of the aromatic-aliphatic polyester (A) is of between 80° and 120° C.

28. A mixture of biodegradable polyesters according to claim **1** in which the molecular weight of the aliphatic polyester (B) is >60,000, and its melting point is of between 50° and 145° C.

29. A mixture of biodegradable polyesters according to claim **1** in which the molecular weight of the aliphatic polyester (B) is >60,000, and its melting point is of between 55° and 130° C.

30. Mixture of biodegradable polyesters according to claim **9** wherein the aliphatic polyester (B) contains as diacid, azelaic acid, sebacic acid, brassilic acid, or mixtures thereof in a concentration, with respect to the total acid content, higher than 70% moles.

31. Film according to claim **15**, characterized by tear resistance in both directions, according to the Elmendorf test, of between 15 and 90 N/mm.

32. Film according to claim **15**, characterized by tear resistance in both directions, according to the Elmendorf test, of between 20 and 80 N/mm.

33. Film according to claim **15** characterized in that the modulus value is of between 250 and 1000 MPa.

34. Mixture of biodegradable polyesters according to claim **1** in which the polyester (B) is of the diacid/diol type selected from the group consisting of polybutylensebacate, polybutylenazelate, polyethylensebacate, polyethylenazelate, polybutylensuccinate, polybutylenbrassilate, polybutylenazelateadipate, polyallcylenbrassilate.

* * * * *

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United States Patent [19]

Lorcks et al.

[11] **Patent Number: 6,096,809**

[45] **Date of Patent: Aug. 1, 2000**

[54] **BIOLOGICALLY DEGRADABLE POLYMER MIXTURE**

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[52] **U.S. Cl.** **524/47**; 524/386; 524/539; 524/605; 525/54.24; 523/128; 528/308.6

[58] **Field of Search** 524/47, 605, 539, 524/386; 525/54.24; 528/308.6; 523/128

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[57] **ABSTRACT**

A biologically degradable polymer mixture contains at least one starch biopolymer made from renewable raw materials, a plasticizer, and a polymer selected from the following materials: an aromatic polyester; a polyester-copolymer with both aliphatic and aromatic blocks; a polyesteramide; a polyglycol; a polyester urethane; and/or mixtures of these components.

30 Claims, No Drawings

BIOLOGICALLY DEGRADABLE POLYMER MIXTURE

The present invention relates to a biologically degradable polymer mixture, to a process for its preparation and to a method of processing the polymer mixture according to the invention.

Proposals for the preparation of biologically degradable polymer mixtures are known from a large number of patent documents and articles. The great problem in the case of polymer mixtures lies, as a rule, in that those mixtures which have an excellent, biological degradability have only limited possibilities for use in the area of engineering plastics, thereby explaining the relatively modest success to date. Polymer mixtures having improved properties are either biologically inadequate or degradable with increased effort, or else are too expensive.

From EP-535 994 a polymer mixture is known essentially consisting of starch and an aliphatic polyester, for example polycaprolactone, where the starch is preferably destructured with water.

Aliphatic polyesters are, per se, suitable mixing components for the preparation of biologically degradable polymer mixtures, since they have a good biological degradability. However, aliphatic polyesters have only moderate material properties, for example with regard to melting point, tensile strength, etc., which is why even corresponding mixtures using a polymer prepared on the basis of renewable raw materials, for example thermoplastic starch, have only moderate properties, thereby again placing in question the possibility for use in the field of engineering plastics.

It is therefore an object of the present invention to propose a biologically degradable polymer mixture which both is flawlessly degradable biologically and in addition has good mechanical and thermal properties, so that use as an engineering plastic or as a polymer material is appropriate. A further prerequisite for suitability as a polymer material also lies in the price for the polymer mixture proposed having an acceptable magnitude.

The multitude of biopolymers or biologically degradable polymer mixtures proposed in the prior art are to a great extent in accordance with object having an acceptable magnitude.

In accordance with the invention the object proposed above is achieved by means of a biologically degradable polymer mixture in accordance with the wording of claim **1**.

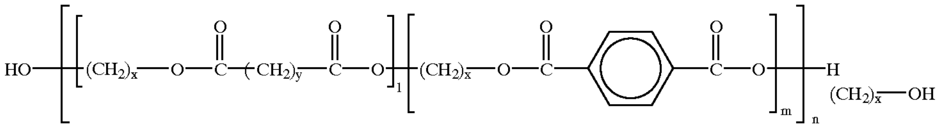
The multitude of biopolymers or biologically degradable polymer mixtures proposed in the prior art are to a great extent constructed on the basis of starch or use starch, although native starch is hardly suitable as a technically usable polymer. Starch is proposed because it is readily degradable biologically, has a favorable price and is independent of petroleum products because it is based on a renewable raw material. Because of the poor suitability of native starch as an "engineering plastic" it is proposed according to the invention to use so-called thermoplastic starch, as is proposed, for example, in PCT/WO90/05161. This thermoplastic starch is obtained by processing native starch in the melt, by means of a plasticizing or swelling

agent, to a homogeneous mass, where the proportion of swelling or plasticizing agent can as a rule amount to between 10 and about 40%, based on the overall weight of the mixture. [As set out in claim **4**,] Suitable swelling or plasticizing agents are, inter alia, for example, glycerol or sorbitol.

Particularly suitable materials for improving the rather moderate material properties of thermoplastic starch include:

The aliphatic polyesters proposed in the prior art, which although having good biological degradability are not particularly suitable because of their likewise moderate material properties with regard to melting point and drawability, themselves contribute to an improvement in the material properties of the thermoplastic starch. In contrast, aromatic polyesters exhibit excellent material properties but their biological degradability is rather moderate. On the other hand, inter alia, polyester copolymers based on aromatic and aliphatic dicarboxylic acids, polyesteramides and also polyesterurethanes have both outstanding material properties and a rapid biological degradability, which is why they are particularly suitable for use in polymer mixtures with thermoplastic starch.

The polyester copolymers proposed for use in accordance with the invention in the polymer mixture with thermoplastic starch are constructed on the basis, besides the customarily used polyols, of aromatic and aliphatic dicarboxylic acids, and have the following general structure:



The polyester copolymers proposed according to the invention can be prepared from petrochemical mass products, such as adipic acid, sebacic acid, terephthalic acid and a diol by means of polycondensation, with commercially customary diols, such as 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol and/or 1,6-hexanediol being used. What is important is that both aromatic and aliphatic dicarboxylic acids are used, by means of which the statistical polyester copolymers are prepared, for example by means of a conventional polycondensation process.

Statistical copolyesters of aliphatic and aromatic dicarboxylic acids with a proportion, for example, of about 35–55 mol % of aromatic acid, for example terephthalic acid, represent an optimum compromise between biological degradability and material properties, as a result of which they are particularly suitable in mixtures with thermoplastic starch. The biological degradability of statistical copolyesters of this kind lies within 8–12 weeks in compost and earth. In this context reference may be made to U.S. Pat. No. 5,446,079, in which the preparation of aliphatic-aromatic copolyesters is described in detail.

Polyalkylene terephthalates and polyethylene terephthalates which are prepared from aliphatic diols and aromatic dicarboxylic acids have proven, for example, to be suitable copolyesters for the preparation of a starch/polyester copolymer blend according to the invention.

In addition to the starch/polyester copolymer blends described above and proposed according to the invention it has become evident that polyesteramides filled or blended with starch or thermoplastic starch and with ester contents of between 30 and 70% by weight have good mechanical properties, even for the production of films, and have good degradability and compostibility. Proposed are, for example, polyesteramides having a mean molecular weight in a range of 10–300,000, preferably 20–150,000. Otherwise reference may be made to the European patent application EP-A-641 817, in which the synthesis of the polyesteramides proposed in accordance with the invention is described in detail. Mention should merely be made that polyesteramides according to the invention can be constructed from monomers of the following groups:

dialcohols, such as ethylene glycol, 1,4-butanediol, 1,3-propanediol, 1,6-hexanediol diethylene glycol and others; and/or

dicarboxylic acid, such as oxalic acid, succinic acid, adipic acid and others, including those in the form of their respective esters (methyl, ethyl etc.); and/or

hydroxycarboxylic acids and lactones, such as caprolactone and others; and/or

amino alcohols, such as ethanolamine, propanolamine etc.; and/or

cyclic lactams, such as E-caprolactam or laurolactam etc.; and/or

ω-aminocarboxylic acids, such as aminocaproic acid etc.: and/or

mixtures (1:1 salts) of dicarboxylic acids such as adipic acid, succinic acid etc. and diamines such as hexamethylenediamine, diaminobutane etc.

In the case where the polymer mixture is based extensively on thermoplastic starch and an aromatic polyester, an aliphatic-aromatic copolyester or a polyesteramide it may be advantageous to add an aliphatic polyester or copolyester, such as polycaprolactone, for example, as a further component. By this means the relatively poor biological degradability, for example, of the aromatic polyester is compensated by the excellent degradability of the aliphatic polyester. As an example of this there may be mentioned a polymer mixture consisting of thermoplastic starch, at least one polyethylene terephthalate (PET) or a polyalkylene terephthalate, and polycaprolactone. Other examples of aliphatic polyesters or copolyesters are polylactic acid, polyhydroxybutyric acid, polyhyroxybenzoic acid, polyhydroxybutyric acid-hydroxy-valeric acid copolymer and/or mixtures thereof.

Depending on how the preparation of the polymer mixture is carried out it is advantageous if this mixture additionally contains a block copolymer as phase mediator in order to form a continuous, homogeneous phase between the thermoplastic starch and the hydrophobic polymer in the form of the polyester. A phase mediator of this kind can, for example, be a reaction mixture obtained by essentially anhydrous mixing of thermoplastic starch or, if desired, native or destructured starch with an aliphatic or aromatic polyester or copolyester, with an aromatic/aliphatic copolyester, with a polyesteramide and/or a polyesterurethane.

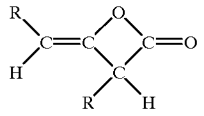
The proportion of thermoplastic starch containing the above-mentioned plasticizing or swelling agent can make up a proportion of between 10–95% by weight, based on the overall weight, in the polymer mixture proposed in accordance with the invention; preferably, 30–75% by weight of thermoplastic starch is used. The proportion of thermoplastic starch depends on the one hand on the polyester or copolyester used and on the other hand on the intended use of the polymer mixture, such as injection molding, extrusion or film blowing. The requirements with regard to the material properties also influence the proportion of thermoplastic starch. If, for example, heightened material requirements with respect to mechanical and thermal properties are imposed, a proportion of thermoplastic starch in the range of 40–65% by weight will preferably be targeted; consequently, the price of the mixture remains acceptable in any case.

Also a subject of the present invention are mixtures containing 90–30, especially 80–40% by weight of thermoplastically processible polyesteramides comprising 30–70% by weight aliphatic esters and 70–30% by weight aliphatic amide structures, where, furthermore, preferably 10–90% by weight, in particular 20–60% by weight of starch or thermoplastic starch are contained.

The addition of further additives, such as plasticizers, stabilizers, antiflaming agents and also further, biologically degradable polymers, such as cellulose esters, cellulose acetate, cellulose, polyhydroxybutyric acid, hydrophobic proteins, polyvinyl alcohol, etc., is possible and again is guided by the requirements with regard to the polymer mixture to be prepared and of course also by the availability of the corresponding components. The polymers indicated below are also suitable as additives, such as gelatins, proteins, zeins, polysaccharides, cellulose derivatives, polylactides, polyvinyl alcohol, polyvinyl acetate, polyacrylates, sugar alcohols, shellac, casein, fatty acid derivatives, plant fibers, lecithin, chitosan, polyesterpolyurethanes and polyesteramides. Mention should also be made of polyester blends consisting of thermoplastic starch, the aliphatic/aromatic polyester proposed according to the invention and, as further component, copolymers selected from ethylene-acrylic acid copolymer and ethylene-vinyl alcohol copolymer.

Also suitable as fillers are, in particular, organic fillers obtained from renewable raw materials, for example cellulose fibers.

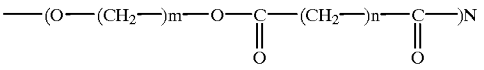
In order to reduce the hydrophilic polymer properties of materials comprising thermoplastic starch it is also possible to add crosslinking agents, for example alkylketene dimers of the following general formula:



where R=linearly saturated alkyl group in the range from C12–C24. The concentration of such network agents amounts as a rule to about 0.05–2%, based on the weight, proportion of dry thermoplastic starch in the polymer mixture, preferably 0.1–1% by weight. The proposed alkylketene dimers react in this case with the hydroxyl groups of the starch polymer.

The preparation of the polymer mixture proposed according to the invention takes place by mixing starch, such as preferably thermoplastic starch, together with the aromatic polyester and/or the polyester copolymer containing aromatic and aliphatic constituents in the melt, the water content in the mixture being reduced before or during mixing to less than 1% by weight, based on the weight of the mixture.

Especially in the case of the exclusive use of an aromatic polyester together with the thermoplastic starch for the preparation of the polymer mixture it has proven advantageous to add, in addition, an aliphatic polyester during the preparation. Examples of suitable aliphatic polyesters are, for example, polycaprolactone, polylactic acid, etc., as already set out above. Further suitable aliphatic polyesters are, for example, polyethylene succinate (PESU) and polybutylene succinate (PBSU). The latter aliphatic polyesters are formed by reaction of glycols with aliphatic dicarboxylic acids and other acids and have the following general structural formula:



$$-(O-(CH_2-)m-O-\underset{\underset{O}{\|}}{C}-(CH_2-)n-\underset{\underset{O}{\|}}{C}-)N$$

In every case it is proposed, in accordance with a preferred variant embodiment of the process according to the invention, to reduce the water content during the mixing of the melt to below 0.5% by weight, preferably even to below 0.1% by weight, based on the overall weight of the mixture.

In the preparation of the polymer mixture proposed in accordance with the invention, the thermoplastic starch is present to begin with as a so-called disperse phase, while the polyester or the copolyester, the polyesteramide or the polyesterurethane, representing a hydrophobic polymer, is present as a substantially coherent, continuous phase. An obvious supposition, then, is that when the two polymers are mixed with the exclusion of water the ester groups incorporated in the molecule chains of the polyester or copolyester, etc. undergo esterification reactions with the thermoplastic starch, as a result of which the molecule chains reacting in this way form a phase mediator with the starch which allows a molecular coupling of the two phases, and consequently a continuous phase is formed. In the case of moisture this reaction is in competition, since in the presence of water the acid ester groups do not react with the starch, to form the phase mediator, but instead are hydrolyzed. This, however, prevents formation of the phase mediator, which renders flawless dispersing or homogenizing impossible. It is of course possible to use a phase mediator from the outset, such as a block copolymer which comprises at least two blocks, one block being at least substantially soluble in the hydrophobic polyester phase and the other block being at least substantially soluble in the starch phase. In this context reference may be made to DE-42 37 535.5.

Depending on the aromatic, aliphatic, aromatic/aliphatic copolyester polyesteramide and/or polyesterurethane used, mixing is conducted in the melt in a temperature range between 120–260° C., preferably in a range of 140–160° C. The mixing temperature must be chosen so that no damage can occur to the polyester or copolyester used. The mixing of the thermoplastic starch with the polyester component or components, together if desired with further additives and components, takes place preferably in an extruder or kneader, which preferably has a devolatilizing device, for the continuous removal of moisture, in order to attain the required freedom from water. It has been found that, when the thermoplastic starch is mixed with the polyester or polyesters, water is formed, which allows one to draw the conclusion of, for example, the above-mentioned reaction of the ester groups with the starch to form the phase mediator. On leaving the extruder or kneader through the die the melt has an extremely low water content, preferably <0.5 or <0.1% by weight. After removal from the die the melt is preferably cooled in a water bath and conditioned before being subjected subsequently granulated, for example. It has proven advantageous if the melt, which is dry per se, is cooled in a water bath so that it absorbs within the order of magnitude of 2—about 6% by weight, based on the overall weight, of water, in order to ensure flawless granulation.

The polymer mixture prepared in accordance with the invention, comprising at least thermoplastic starch and, for example, the polyester copolymer comprising aromatic and aliphatic blocks, is outstandingly suitable as a polymer material for a very wide variety of applications in the field of so-called “engineering plastics”. Processing in the injection molding process, as well as by extrusion and film blowing, is possible, for instance. However, when processing the polymer mixture according to the invention it has been found advantageous if the polymer mixture, which is present for example as granules, is conditioned before processing, either by means of water or with a plasticizer, such as glycerol or a mixture thereof. The target is, for example, a water content of about 1–6% by weight, based on the overall weight, preferably 3–5% by weight, as is usual, for example, in the processing of polyesters. Also, the injection moldings, extrudates or films produced are preferably stored directly after their preparation in an environment having a relative humidity of at least 40%, preferably at least 45–50%.

Examples of possible and preferred polymer mixtures, exhibiting at least starch or thermoplastic starch and a hydrophobic polymer as claimed in one of the dependent claims **2**–**15** or prepared in accordance with a process set out in one of claims **16**–**22** are listed in Tables 1–4 depicted below. These examples are supplemented by an additional experiment 29.

The total of 29 examples indicated in this case include both components which have been used for the preparation of thermoplastic starch in the sense of plasticizing agents or swelling agents and the possible polymeric mixing partners to the thermoplastic starch for the preparation of the polymer mixtures proposed in accordance with the invention. The tables include, moreover, the processing conditions and, in particular, the water content in the extruder which prevails during the preparation of the polymer mixture, and which without exception amounted to <than 0.1% by weight. In addition, preferred application options for the polymer mixtures prepared by way of example are set out in the tables. The tables of course contain only examples, and all components mentioned at the outset are suitable for mixing with starch or thermoplastic starch for preparing starting polymer mixtures, defined in accordance with the invention, for both technical and nontechnical applications.

TABLE 1

	Examples						
Example	1	2	3	4	5	6	7
^{1}Starch %	42.2	24.0	29.9	24.0	33.0	38.0	21.5
^{1}Sorbitol %	14.0	8.0	9.5	8.0	9.9	11.8	6.9
^{1}Glycerol %	9.5	6.0	6.5	6.0	7.9	9.3	2.1
^{2}TPS %	60.5	34.9	42.0	34.9	46.7	54.5	27.8

TABLE 1-continued

Example	Examples 1	 2	 3	 4	 5	 6	 7
H_2O %	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
[3]PLA %	—	—	—	—	40.0	10.9	—
[4]Polyamide 1	34.3	50.0	—	—	9.2	—	69.5
[5]Polyester 1	—	—	54.1	45.0	—	30.0	—
[6]PCL %	—	12.0	—	17.0	—	—	—
H_2O %	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
[7]Extrusion	ZSK 40	ZSK 40	ZSK 40	ZSK 40	ZSK 40	ZSK 40	ZSK 40
T ° C.	212	225	210	210	215	210	200
Pressure bar	8.5	2.0	2.5	2.5	6.2	7.5	0.5
MFI g/10'	9	13	11.5	13	8.5	8.0	29
Granules	4 mm	4 mm	4 mm	4 mm	4 mm	4 mm	4 mm
Gra H_2O %	3.0	3.6	3.4	3.6	3.4	3.4	3.0
Application							
Blown film	+	+	+	+	+	+	–
Flat film	+	+	+	+	+	+	–
Sheets	+	+	+	+	+	+	–
Injection molding	+	–	–	–	–	–	–
Fibers	–	+	–	+	–	–	+

[1] Starch = native potato starch dried 3.5% H_2O, sorbitol = sorbitol LG DHR 71%, glycerol 99.5%;
[2] TPS = thermoplastic starch = starch + sorbitol + glycerol < 0.1% H_2O. — Water content by devolatilization, according to the known process EP 0 397 819 anhydrous TPS consists of starch, sorbitol and glycerol;
[3] PLA (polylactic acid resin) — Mitsui Toatsu Chemicals LACEA H 100 MFR 13 190° C. 2.16 kg:
[4] Polyamide 1 = Bayer BAK 1095 polyersteramide MFI 2.5 150° C. 2.16 kg;
[5] Polyester 1 = BASF ZK 242/108 copolyester of aliphatic diols and aliphatic/aromatic dicarboxylic acids MVR 3.0 at 190° C./2.16 kg;
[6] PCL (polycaprolactone) + Union Carbide Tone Polymer P-787 MFI 1.0 125° C. 44 psi g/10 min;
[7] Extrusion Equipment = Werner & Pfleiderer ZSK 40;
*0.1–0.4% water content

TABLE 2

Example	Examples 8	 9	 10	 11	 12	 13	 14
[1]Starch %	38.2	24.6	29.2	24.6	30.7	28.0	21.5
[1]Sorbitol %	12.8	8.2	9.4	8.8	9.1	8.8	6.9
[1]Glycerol %	8.5	6.0	6.2	6.0	7.4	6.2	4.1
[2]TPS %	54.5	35.5	41.1	36.0	43.5	39.5	29.7
H_2O %	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
[3]PPDX %	34.0	—	—	6.5	—	—	33.8
[4]PT-C300	—	—	45.1	—	—	—	—
[5]PT-T8-200	—	32.5	—	—	47.0	57.0	—
[6]BAK	6.5	28.7	10.1	54.1	5.8	—	33.7
H_2O %	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
[7]Extrusion	ZSK 40	ZSK 40	ZSK 40	ZSK 40	ZSK 40	ZSK 40	ZSK 40
T ° C.	220	214	240	215	215	210	205
Pressure bar	6.5	3.5	5.5	7.5	4.5	7.5	0.5
MFI g/10'	8	13	2.5	11.5	8.5	8.0	30
Granules	4 mm	4 mm	4 mm	4 mm	4 mm	4 mm	4 mm
Gra H_2O %	3.9	3.6	3.5	3.3	3.4	3.6	3.2
Application							
Blown film	+	+	+	+	+	+	–
Flat film	+	+	+	+	+	+	–
Sheets	+	+	+	+	+	+	–
Injection molding	+ <0.15*	–	+ <0.4*	–	–	–	–
Fibers	–	–	–	–	–	–	+

[1] Starch = native potato starch dried 3.5% H_2O, sorbitol = sorbitol LG DHR 71%, glycerol 99.5%;
[2] TPS = thermoplastic starch = starch + sorbitol + glycerol < 0.1% H_2O. — Water content by devolatilization, according to the known process EP 0 397 819 anhydrous TPS consists of starch, sorbitol and glycerol;
[3] PPDX. Polyparadioxanone. Shell International Chemicals Ltd. peak melting deg ° C. 110.;
[4] PT-C300ZT. Enviro Plastic, Plantet Polymers, VICAT Softening Temp. 89° C. Polyethylene oxide polymers;

TABLE 2-continued

Example	Examples 8	9	10	11	12	13	14

[5] PT-T8-200DL. Enviro-Plastic C. Planet Polymers, Polyethylene oxide polymers;

[6] Polyesteramide BAK 1095, Bayer AG, MFI 2.5 150° C., 2.16 kg;

[7] Extrusion Equipment = Werner & Pfleiderer ZSK 40;

*0.1–0.4% water content

TABLE 3

Example	Examples 15	16	17	18	19	20	21
^{1}Starch %	20.9	24.6	20.4	24.6	9.2	9.2	9.2
^{1}Sorbitol %	7.0	8.2	6.6	8.8	2.7	2.7	2.7
^{1}Glycerol %	4.7	6.0	4.4	6.0	2.2	2.2	2.2
^{2}TPS %	29.9	35.5	28.6	36.0	13.0	13.0	13.0
H_2O %	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
^{3}Filler %	26.9	—	25.0	—	60.0	—	60.0
^{4}Polyamide 1	40.5	36.2	—	—	25.9	27.9	—
^{5}Polyester 1	—	—	43.6	35.6	—	—	25.9
^{6}Filler %	—	25.0	—	25.0	—	58.0	—
H_2O %	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
^{7}Extrusion	ZSK 40	ZSK 40	ZSK 40	ZSK 40	ZSK 40	ZSK 40	ZSK 40
T ° C.	203	206	220	21S	205	20S	220
Pressure bar	156.5	21	15	22	3S	40	35
MFI g/10'	13	9	12.5	8.5	3	2.8	2.2
Granules	4 mm	4 mm	4 mm	4 mm	4 mm	4 mm	4 mm
Gra H_2O %	3.5	3.6	3.4	3.6	3.4	3.4	3.0
Application							
Blown film	–	–	–	–	–	–	–
Flat film	(+)	(+)	(+)	(+)	–	–	–
Sheets	+	+	+	+	+	+	+
Injection	+	+	+	+	+	+	+
molding	<0.2%*	<0.2%*	<0.2%*	<0.2%*	<0.2%*	<0.2%*	<0.2%*
Fibers	–	–	–	–	–	–	–

[1] Starch = native potato starch dried 3.5% H_2O, sorbitol = sorbitol LG DHR 71%, glycerol 99.5%;

[2] TPS = thermoplastic starch = starch + sorbitol + glycerol < 0.1% H_2O. — Water content by devolatilization, according to the known process EP 0 397 819 anhydrous TPS consists of starch, sorbitol and glycerol;

[3] Filler, microized cellulose;

[4] Polyamide 1 = Bayer BAK 1095 polyersteramide MFI 2.5 150° C. 2.16 kg;

[5] Polyester 1 = BASF ZK 242/108 copolyester of aliphatic diols and aliphatic/aromatic dicarboxylic acids MVR 3.0 at 190° C./2.16 kg;

[6] Filler, micronized cotton

[7] Extrusion Equipment = Werner & Pfleiderer ZSK 40;

*0.1–0.4% water content

TABLE 4

Example	Examples 22	23	24	25	26	27**	28**
^{1}Starch %	34.5	35.5	40.5	50.5	60.7	70.3	67.8
^{1}Sorbitol %	—	—	—	—	—	—	—
^{1}Glycerol %	16.3	16.5	12.0	7.1	4.0	4.5	—
^{2}Polyamide 1	25.0	23.5	47.5	42.4	35.3	25.2	32.2
^{3}TPS %	74.8	74.4	98.6	98.5	98.2	87.4	87.8
H_2O %	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
^{4}PLA %	24.2	—	—	—	—	—	—
^{5}Polyester 1	—	24.5	—	—	—	—	—
^{6}	—	—	—	—	—	—	—
H_2O %	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
^{7}Extrusion	ZSK 40	ZSK 40	ZSK 40	ZSK 40	ZSK 40	ZSK 40	ZSK 40
T ° C.	200	206	190	170	160	155	155
Pressure bar	15	15	20	26	31	35	37
MFI g/10'	12	14	122.5	10	6	5	5.5
Granules	4 mm	4 mm	4 mm	4 mm	4 mm	4 mm	4 mm
Gra H_2O %	2.1	2.1	2.2	2.6	0.4	0.4	0.3

TABLE 4-continued

	Examples						
Example	22	23	24	25	26	27**	28**
Application							
Blown film	+	+	+	+	+	+	+
Flat film	+	+	+	+	+	+	+
Sheets	+	+	+	+	+	+	+
Injection molding	–	–	–	(+)	+ <0.15%*	+ <0.2%*	+ <0.2%*
Fibers	–	–	–	–	–	–	–

[1] Starch = native potato starch dried 3.5% H_2O, sorbitol = sorbitol LG DHR 71%, glycerol 99.5%;

[4] Polyamide 1 = Bayer BAK 1095 polyersteramide MFI 2.5 150° C. 2.16 kg, function of plasticizer;

[2] TPS = thermoplastic starch = starch + sorbitol + glycerol and/or BAK 1095, <0.1% H_2O. — Water content by devolatilization, according to the known process EP 0 397 819. 27** + 28** starch = native potato starch, 18% H_2O:

[3] PLA (Polylactic acid resin) = Mitsui Toatsu Chemicals LACEA H 100 MFR 13 190° C. 2.16 kg;

[5] Polyester 1 = BASF ZK 242/108 copolyester of aliphatic diols and aliphatic/aromatic dicarboxylic acids MVR 3.0 at 190° C./2.16 kg;

[6] PCL (Polycaprolactone) + Union Carbide Tone Polymer P-787 MFI 1.0 125° C. 44 psi g/10 min;

[7] Extrusion Equipment = Werner & Pfleiderer ZSK 40;

*0.1–0.4% water content

EXPERIMENT EXAMPLE 29

In analogy to experiment 28, the polyesteramide BAK 1095 was in example 29 compounded with 10% potato starch in the twin-screw extruder ZSK 40 at 155° C. and 20 bar with removal of water, extruded with 0.15% residual moisture, and, after the polyester extrudate had cooled, was granulated. The polymer mixture has an MFI g/10' of 25 at 150° C./5 kg and is suitable for producing blown and flat films.

Injection moldings, extrudates and films produced by means of polymer mixtures proposed in accordance with the invention have not only relatively good material properties but also an outstanding biological degradability, which is why they are able to make a significant contribution to the acute problem of waste. For example, films produced from a polymer mixture proposed in accordance with the invention are outstandingly suitable for a very wide variety of applications in the agricultural sector, for example for the covering of fields, since such films after their use can either be composted or else ploughed into the earth in the field. Polymer mixtures of this kind are also suitable for the production of composting sacks, containers for composting waste, etc. In addition, containers and bottles, for example, can be produced from the polymer mixture proposed in accordance with the invention by means of blow molding.

The polymer mixtures according to the invention are also suitable, however, for the production of textile articles, for example for the production of fibers, monofilaments, sheetlike structures, such as wovens, felts, nonwovens, so-called backsheets, textile composites, flocks, wadding, and linear structures, for example filaments, yarns, cables, cords, etc. In particular it has been found in practice that the polymer mixtures according to the invention are suitable for the production of sanitary articles, such as diapers, sanitary towels, incontinence products and bed liners. The structure of these hygiene articles includes, inter alia, nonwovens produced from the polymer material according to the invention, since this material has a very good skin compatibility, is respiratorily active, is permeable to water vapor at the same time as being watertight, and yet is fully biologically degradable.

A large proportion of the polymer mixtures proposed in accordance with the invention, especially those containing thermoplastic starch and/or a copolyester and/or a polyesteramide and/or a polyesterurethane, are suitable, moreover, as adhesives or else can be used as coatings, for example for the impregnation of textile wovens. In this case it has been found that the polymer mixtures proposed in accordance with the invention which are suitable for these areas of application are introduced and applied preferably in a form in which they are at least partially dissolved in alcoholic solvents. For example, in connection with experiment example 29 it was found, surprisingly, that the polymer mixture thus prepared is soluble in hot alcohol/ethanol mixture. A 20% strength alcoholic solution directly after preparation has a viscosity of 100^{n} Pas. In this case too there was a possible use in the context of a biologically degradable adhesive, as a coating or as an impregnation which brings about hydrophobic properties and is permeable to water vapor. The use ascertained with regard to experiment example 29 can also be transferred to a large number of the other experiment examples and to further polymer mixtures proposed in accordance with the invention.

The polymer mixtures according to the invention are, however, of course suitable for umpteen other applications, for example for disposable injection-molded products, etc.

We claim:

1. A composition of matter that is at least partially biodegradable comprising:

thermoplastic starch formed by mixing starch and at least one plasticizing agent under conditions that result in the formation of a thermoplastic melt so that the thermoplastic melt has a water content of less than 5% while in a melted state, wherein the plasticizing agent is selected from the group consisting of glycerin, sorbitol, sugar alcohols, hydroxy acids, playvinyl alcohol, and mixtures thereof; and

at least one polymer selected from the group consisting of aromatic polyesters, polyester copolymers having both aliphatic and aromatic blocks, polyester amides, polyethylene oxide polymers, polyglycols, and polyester urethanes, wherein the composition is formed by melting and mixing the thermoplastic starch and the at least one polymer under conditions that reduce or maintain the water content of the composition at less than about 1% by weight while in a melted state.

2. A composition of matter as defined in claim **1** formed by melting and mixing the thermoplastic starch and the at least one polymer under conditions that reduce or maintain the water content of the composition at less than about 0.5% by weight while in a melted state.

3. A composition of matter as defined in claim **1** formed by melting and mixing the thermoplastic starch and the at least one polymer in a manner so as to reduce or maintain the water content of the composition at less than about 0.1% by weight while in a melted state.

4. A composition of matter as defined in claim **1**, wherein the polymer comprises a polyester copolymer of at least one polyol and at least one aromatic dicarboxylic acid.

5. A composition of matter as defined in claim **4**, wherein the polyol is selected the group consisting of 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, and mixtures thereof, and wherein the aromatic dicarboxylic acid is a terephthalate and, optionally, adipic acid or sebacic acid or both.

6. A composition of matter as defined in claim **1**, wherein the polymer is a polyester copolymer of at least one polyol, at least one aromatic dicarboxylic acid and at least one aliphatic dicarboxylic acid.

7. A composition of matter as defined in claim **6**, wherein the polyester copolymer is a polyalkylene terephthalate.

8. A composition of matter as defined in claim **1**, further comprising at least one aliphatic polyester or copolyester.

9. A composition of matter as defined in claim **8**, wherein the aliphatic polyester or copolyester comprises polycaprolactone.

10. A composition of matter as defined in claim **1**, further comprising at least one additional component selected from the group consisting of additional plasticizers, stabilizers, antiflaming agents, additional biologically degradable biopolymers, organic fillers, and cross-linking agents.

11. A composition of matter as defined in claim **1**, wherein the thermoplastic starch is included in an amount in a range from about 10% to about 95% by weight of the composition.

12. A composition of matter as defined in claim **1**, wherein the thermoplastic starch is included in an amount in a range from about 30% to about 65% by weight of the composition.

13. A composition of matter as defined in claim **1**, further comprising at least one additional polymer selected from the group consisting of ethylene/acrylic acid copolymer and ethylene/vinyl alcohol copolymer.

14. A composition of matter as defined in claim **1**, wherein the composition is formed by mixing and melting the thermoplastic starch and the at least one polymer at a temperature in a range from about 120° C. to about 260° C.

15. A composition of matter as defined in claim **1**, wherein the composition is formed by melting and mixing the thermoplastic starch and the at least one polymer in an extruder or kneader and wherein the composition is discharged from the extruder or kneader while in a melted state and subsequently cooled to a substantially solidified state and conditioned so as to reabsorb water.

16. A composition of matter as defined in claim **15**, wherein the composition is conditioned so as to include a water content in a range from about 1% to about 6% by weight of the substantially solidified composition.

17. A composition of matter as defined in claim **15**, wherein the conditioned composition is in the form of a granulate.

18. A composition of matter as defined in claim **15**, wherein the composition is conditioned so as to include a water content in a range from about 3% to about 5% water by weight of the substantially solidified composition.

19. A composition of matter as defined in claim **1**, wherein the thermoplastic starch is formed from starch that has been initially predried to below its natural water content.

20. A composition of matter as defined in claim **1**, wherein the thermoplastic starch is formed from starch that initially includes its natural water content, wherein the natural water content of the starch is reduced while the thermoplastic starch is in a melted state.

21. A composition of matter that is at least partially biodegradable comprising:

thermoplastic starch formed by mixing starch and at least one plasticizing agent under conditions that result in the formation of a thermoplastic melt so that the thermoplastic melt has a water content of less than 5% while in a melted state, wherein the plasticizing agent is selected from the group consisting of glycerin, sorbitol, sugar alcohols, and mixtures thereof; and

at least one polymer selected from the group consisting of aromatic polyesters, polyester copolymers having both aliphatic and aromatic blocks, polyester amides, polyethylene oxide polymers, polyglycols, and polyester urethanes,

wherein the composition is formed by melting and mixing the thermoplastic starch and the at least one polymer under conditions that reduce or maintain the water content of the composition at less than about 1% by weight while in a melted state.

22. A composition of matter as defined in claim **21**, wherein the thermoplastic starch is formed from starch that has been initially predried to below its natural water content.

23. A composition of matter as defined in claim **21**, wherein the thermoplastic starch is formed from starch that initially includes its natural water content, wherein the natural water content of the starch is reduced while the thermoplastic starch is in a melted state.

24. A composition of matter that is at least partially biodegradable comprising:

thermoplastic starch formed by mixing starch and at least one plasticizing agent under conditions that result in the formation of a thermoplastic melt so that the thermoplastic melt has a water content of less than 5% while in a melted state, wherein the plasticizing agent is selected from the group consisting of glycerin, sorbitol, sugar alcohols, hydroxy acids, polyvinyl alcohol, and mixtures thereof;

at least one polymer selected from the group consisting of aromatic polyesters, polyester copolymers having both aliphatic and aromatic blocks, polyester amides, polyethylene oxide polymers, polyglycols, and polyester urethanes; and

a phase mediator comprising at least one condensation reaction product of the thermoplastic starch and the at least one polymer,

wherein the composition is formed by melting and mixing the thermoplastic starch and the at least one polymer under conditions that reduce or maintain the water content of the composition at less than about 1% by weight while in a melted state.

25. A composition of matter as declined in claim **24**, wherein the thermoplastic starch is formed from starch that has been initially predried to below its natural water content.

26. A composition of matter as defined in claim **24**, wherein the thermoplastic starch is formed from starch that initially includes its natural water content, wherein the natural water content of the starch is reduced while the thermoplastic starch is in a melted state.

27. A composition of matter as defined in claim **24**, wherein the composition, after being mixed and melted, is cooled with water so as to substantially solidify the composition and allowed to reabsorb water so that the substantially solidified composition has a water content in a range from about 1% to about 6% by weight.

28. A composition of matter that is at least partially biodegradable comprising:

thermoplastic starch formed by mixing starch an at least one plasticizing agent under conditions that result in the formation of a thermoplastic melt so that the thermoplastic melt has a water content of less than 5% while in a melted state, wherein the plasticizing agent is selected from the group consisting of glycerin, sorbitol, sugar alcohols, hydroxy acids, polyvinyl alcohol, and mixtures thereof; and

at least one polyesters copolymer having both aliphatic and aromatic blocks,

wherein the composition is formed by first melting and mixing the thermoplastic starch and the at least one polymer under conditions that reduce or maintain the water content of the composition at less than about 1% by weight while in a melted state, followed by cooling the melted composition with water in order to substantially solidify the composition and allowing it to reabsorb water so that the substantially solidified composition has a final water content in a range from about 1% to about 6% by weight.

29. A composition of matter as defined in claim **27**, wherein the thermoplastic starch is formed from starch that has been initially predried to below its natural water content.

30. A composition of matter as defined in claim **27**, wherein the thermoplastic starch is formed from starch that initially includes its natural water content, wherein the natural water content of the starch is reduced while the thermoplastic starch is in a melted state.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 6,096,809
DATED : August 1, 2000
INVENTOR(S) : Jurgen Lorcks; Winifried Pommeranz; Harald Schmidt

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 7,
Table 1, under the heading “1” approximately 17 lines down, after: “Injection molding” change “+” to -- + <.4%* --

Column 9,
Table 3, under the heading “18” and “20”, to the right of “T°C”: change “21S” to -- 215 -- and change “20S” to -- 205 --
Table 3, under the heading “19”, to the right of “Pressure Bar” change “3S” to -- 35 --
Beneath Table 3, after “[3]Filler,” change “microized” to -- micronized --

Column 11,
Under Table 4, after “[6]PCL (Polycaprolactone)” change “+” to -- = --

Column 12,
Line 61, after “acids,” change “playvinyl” to -- polyvinyl --

Column 14,
Line 63, after “as” change “declined” to -- defined --

Column 15,
Line 12, after “starch” change “an” to -- and --
Line 20, after “one” change “polyesters” to -- polyester --

Signed and Sealed this

Eighteenth Day of December, 2001

Attest:

JAMES E. ROGAN
Director of the United States Patent and Trademark Office

Attesting Officer

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(54) **POLYHYDROXYALKANOATE BIOPOLYMER COMPOSITIONS**

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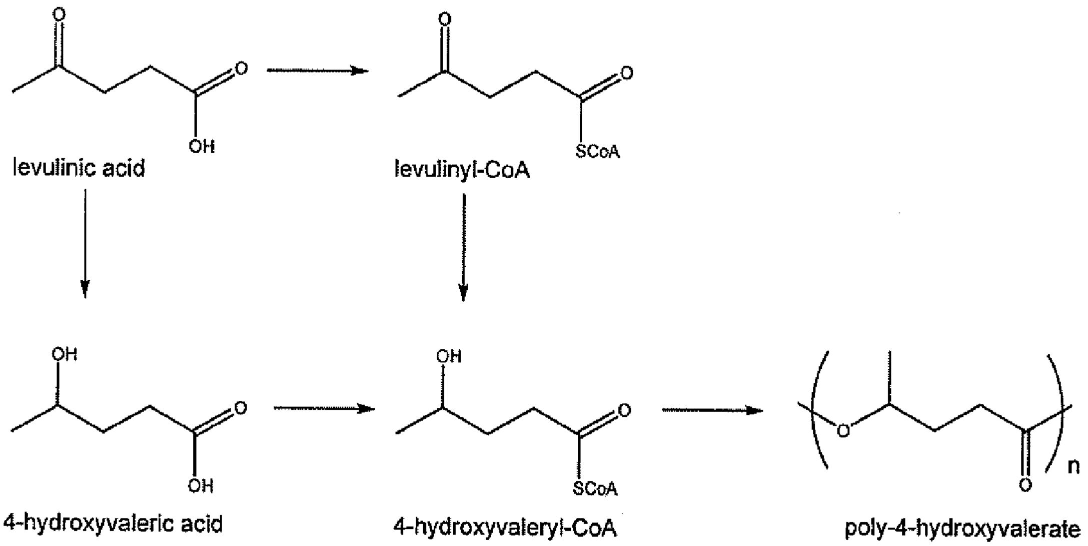
(57) **ABSTRACT**

Several novel PHA polymer compositions produced using biological systems include monomers such as 3-hydroxybutyrate, 3-hydroxypropionate, 2-hydroxybutyrate, 3-hydroxyvalerate, 4-hydroxybutyrate, 4-hydroxyvalerate and 5-hydroxyvalerate. These PHA compositions can readily be extended to incorporate additional monomers including, for example, 3-hydroxyhexanoate, 4-hydroxyhexanoate, 6-hydroxyhexanoate or other longer chain 3-hydroxyacids containing seven or more carbons. This can be accomplished by taking natural PHA producers and mutating through chemical or transposon mutagenesis to delete or inactivate genes encoding undesirable activities. Alternatively, the strains can be genetically engineered to express only those enzymes required for the production of the desired polymer composition. Methods for genetically engineering PHA producing microbes are widely known in the art (Huisman and Madison, 1998, Microbiology and Molecular Biology Reviews, 63: 21-53). These polymers have a variety of uses in medical, industrial and other commercial areas.



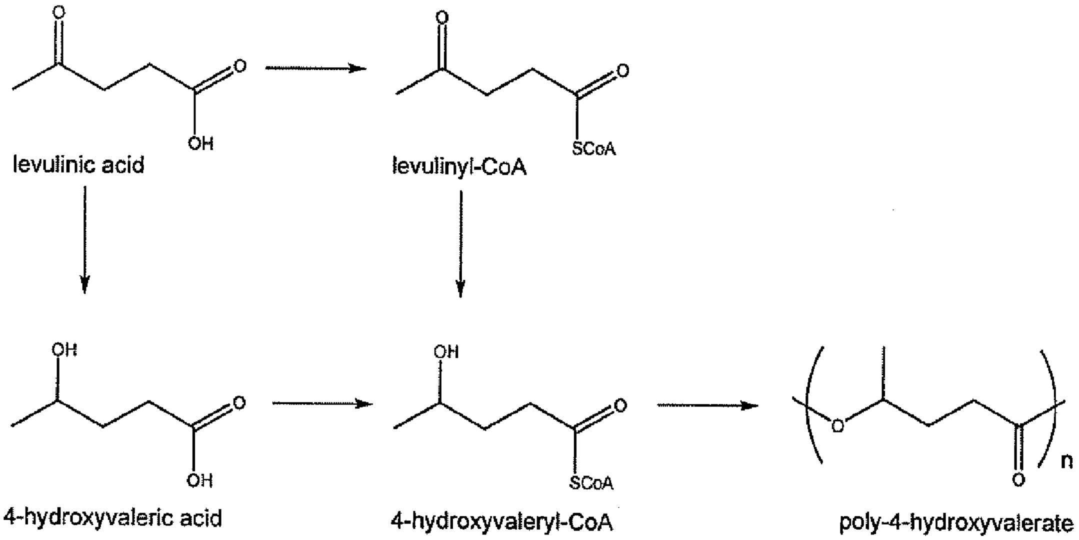
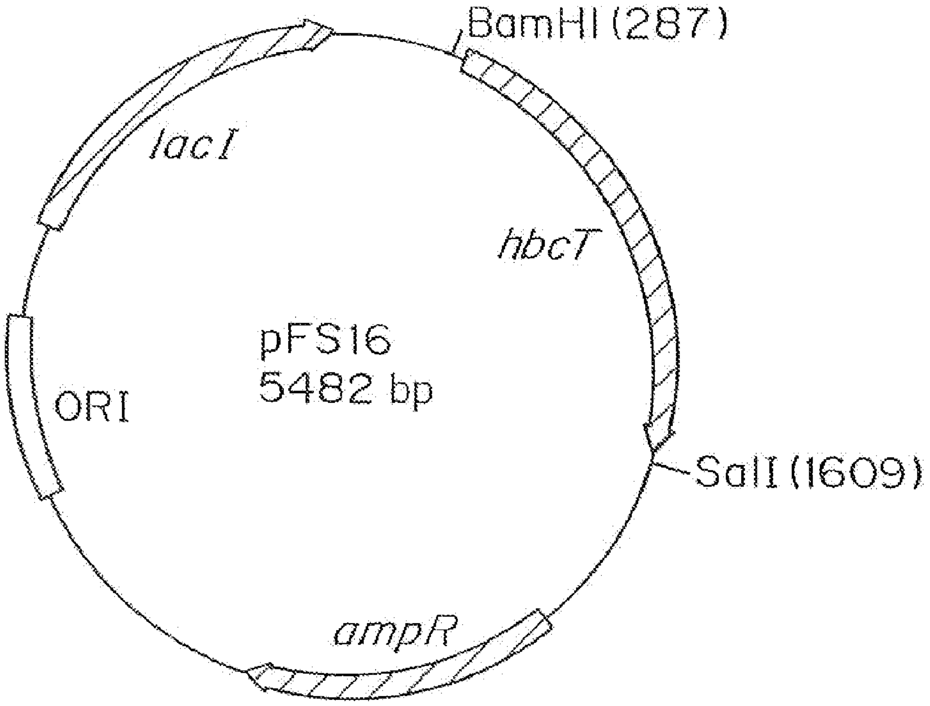

levulinic acid
levulinyl-CoA
4-hydroxyvaleric acid
4-hydroxyvaleryl-CoA
poly-4-hydroxyvalerate

Figure 1

FIG. 2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hbcT
pFS16
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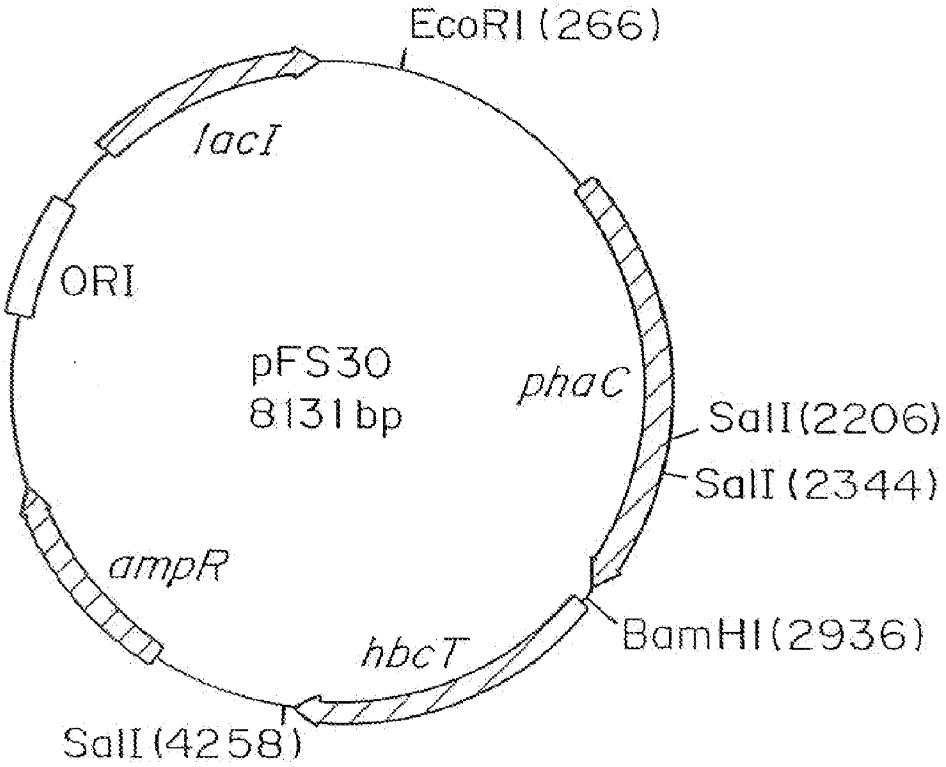
ORI
SalI (1609)
ampR

FIG. 3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lacI
ORI
pFS30
8131 bp
phaC
SalI (2206)
SalI (2344)
ampR
BamHI (2936)
hbcT
SalI (4258)

POLYHYDROXYALKANOATE BIOPOLYMER COMPOSITIONS

[0001] This application claims priority to U.S. Ser. No. 60/086,396 filed May 22, 1998.

BACKGROUND TO THE INVENTION

[0002] Numerous microorganisms have the ability to accumulate intracellular reserves of PHA polymers. Poly [(R)-3-hydroxyalkanoates] (PHAs) are biodegradable and biocompatible thermoplastic materials, produced from renewable resources, with a broad range of industrial and biomedical applications (Williams and Peoples, 1996, CHEMTECH 26, 38-44). Around 100 different monomers have been incorporated into PHA polymers, as reported in the literature (Steinbüehel and Valentin, 1995, FEMS Microbiol. Lett. 128; 219-228) and the biology and genetics of their metabolism has recently been reviewed (Huisman and Madison, 1998, Microbiology and Molecular Biology Reviews, 63: 21-53).

[0003] To date, PHAs have seen limited commercial availability, with only the copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) being available in development quantities. This copolymer has been produced by fermentation of the bacterium *Ralstonia eutropha*. Fermentation and recovery processes for other PHA types have also been developed using a range of bacteria including *Azotobacter, Alcaligenes latus, Comamonas testosterone* and genetically engineered *E. coli* and *Klebsiella* and have recently been reviewed (Braunegg et al., 1998, Journal of Biotechnology 65: 127-161; Choi and Lee, 1999, Appl. Microbiol. Biotechnol. 51: 13-21). More traditional polymer synthesis approaches have also been examined, including direct condensation and ring-opening polymerization of the corresponding lactones (Jesudason and Marchessault, 1994, Macromolecules 27: 2595-2602).

[0004] Synthesis of PHA polymers containing the monomer 4-hydroxybutyrate (PHB4HB, Doi, Y. 1995, Macromol. Symp. 98, 585-599) or 4-hydroxyvalerate and 4-hydroxyhexanoate containing PHA polyesters have been described (Valentin et al., 1992, Appl. Microbiol. Biotechnol. 36, 507-514 and Valentin et al., 1994, Appl. Microbiol. Biotechnol. 40, 710-716). These polyesters have been manufactured using methods similar to that originally described for PHBV in which the microorganisms are fed a relatively expensive non-carbohydrate feedstock in order to force the incorporation of the monomer into the PHA polyester. The PHB4HB copolymers can be produced with a range of monomer compositions which again provides a range of polymer (Saito, Y, Nakamura, S., Hiramitsu, M. and Doi, Y., 1996, Polym. Int. 39: 169).

[0005] PHA copolymers of 3-hydroxybutyrate-co-3-hydroxypropionate have also been described (Shimamura et. al., 1994, Macromolecules 27: 4429-4435; Cao et. al., 1997, Macromol. Chem. Phys. 198: 3539-3557). The highest level of 3-hydroxypropionate incorporated into these copolymers 88 mol % (Shimamura et. al., 1994, Macromolecules 27: 4429-4435).

[0006] PHA terpolymers containing 4-hydroxyvalerate have been produced by feeding a genetically engineered *Pseudomonas putida* strain on 4-hydroxyvalerate or levulinic acid which resulted in a three component PHA, Poly(3-hydroxybutyrate-co-3-hydroxyvalerate-4-hydroxyvalerate) (Valentin et. al., 1992, Appl. Microbiol. Biotechnol. 36: 507-514; Steinbüchel and Gorenflo, 1997, Macromol. Symp. 123: 61-66). It is desirable to develop biological systems to produce two component polymers comprising 4-hydroxyvalerate or poly(4-hydroxyvalerate) homopolymer. The results of Steinbüchel and Gorenflo (1997, Macromol. Symp. 123: 61-66) indicate that *Pseudomonas putida* has the ability to convert levulinic acid to 4-hydroxyvalerate.

[0007] Hein et al. (1997) attempted to synthesize poly-4HV using transgenic *Escherichia coli* strain XL1-Blue but were unsuccessful. These cells carried a plasmid which permitted expression of the *A. eutrophus* PHA synthase and the *Clostridium kluyveri* 4-hydroxybutyryl-CoA transferase genes. When the transgenic *E. coli* were fed 4HV, □-valerolactone, or levulinic acid, they produced only a small amount of PHB homopolymer.

[0008] It is clearly desirable for industrial reasons to be able to produce a range of defined PHA homopolymer, copolymer and terpolymer compositions. To accomplish this, it is desirable to be able to control the availability of the individual enzymes in the corresponding PHA biosynthetic pathways.

[0009] It is therefore an object of the present invention to provide a range of defined PHA homopolymer, copolymer and terpolymer compositions.

[0010] It is another object of the present invention to provide a method and materials to control the availability of the individual enzymes in the corresponding PHA biosynthetic pathways.

SUMMARY OF THE INVENTION

[0011] Several novel PHA polymer compositions produced using biological systems include monomers such as 3-hydroxybutyrate, 3-hydroxypropionate, 2-hydroxybutyrate, 3-hydroxyvalerate, 4-hydroxybutyrate, 4-hydroxyvalerate and 5-hydroxyvalerate. These PHA compositions can readily be extended to incorporate additional monomers including, for example, 3-hydroxyhexanoate, 4-hydroxyhexanoate, 6-hydroxyhexanoate or other longer chain 3-hydroxyacids containing seven or more carbons. This can be accomplished by taking natural PHA producers and mutating through chemical or transposon mutagenesis to delete or inactivate genes encoding undesirable activities. Alternatively, the strains can be genetically engineered to express only those enzymes required for the production of the desired polymer composition. Methods for genetically engineering PHA producing microbes are widely known in the art (Huisman and Madison, 1998, Microbiology and Molecular Biology Reviews, 63: 21-53). These polymers have a variety of uses in medical, industrial and other commercial areas.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. **1** is a schematic of the pathway from levulinic acid to poly-4-hydroxyvalerate.

[0013] FIG. **2** is a schematic of a construct of plasmid pFS16, which includes the lacl (inducer) gene, ampicillin resistance gene, and hbcT gene.

[0014] FIG. **3** is a schematic of a construct of plasmid pFS30, which includes the lacl (inducer) gene, ampicillin resistance gene, polyhydroxyalkanoate polymerase (phaC) gene, and hbcT gene.

DETAILED DESCRIPTION OF THE INVENTION

[0015] Several novel PHA polymer compositions have been produced using biological systems to incorporate monomers such as 3-hydroxybutyrate, 3-hydroxypropionate, 2-hydroxybutyrate, 3-hydroxyvalerate, 4-hydroxybutyrate, 4-hydroxyvalerate and 5-hydroxyvalerate. These PHA compositions can readily be extended to incorporate additional monomers including, for example, 3-hydroxyhexanoate, 4-hydroxyhexanoate, 6-hydroxyhexanoate or other longer chain 3-hydroxyacids containing seven or more carbons. Techniques and procedures to engineer transgenic organisms that synthesize PHAs containing one or more of these monomers either as sole constituent or as co-monomer have been developed. In these systems the transgenic organism is either a bacterium eg. *Escherichia coli, K. pneumoniae, Ralstonia eutropha* (formerly *Alcaligenes eutrophus*), *Alcaligenes lotus* or other microorganisms able to synthesize PHAs, or a higher plant or plant component, such as the seed of an oil crop (Brassica, sunflower, soybean, corn, safflower, flax, palm or coconut or starch accumulating plants (potato, tapioca, cassava).

[0016] It is crucial for efficient PHA synthesis in recombinant *E. coli* strains that the expression of all the genes involved in the pathway be adequate. To this end, the genes of interest can be expressed front extrachromosomal DNA molecules such as plasmids, which intrinsically results in a copy number effect and consequently high expression levels, or, more preferably, they can be expressed from the chromosome. For large scale fermentations of commodity type products it is generally known that plasmid-based systems are unsatisfactory due to the extra burden of maintaining the plasmids and the problems of stable expression. These drawbacks can be overcome using chromosomally encoded enzymes by improving the transcriptional and translational signals preceding the gene of interest such that expression is sufficient and stable.

[0017] The biological systems must express one or more enzymes as required to convert the monomers into polymers. Suitable substrates include 3-hydroxybutylate, 3-hydroxypropionate, 2-hydroxybutyrate, 3-hydroxyvalerate, 4-hydroxybutyrate, 4-hydroxyvalerate, 5-hydroxyvalerate, 3-hydroxyhexanoate, 4-hydroxyhexanoate, 6-hydroxyhexanoate and other longer chain 3-hydroxyacids containing seven or more carbons. These enzymes include polyhydroxyalkanoate synthase, acyl-CoA transferase and hydroxyacyl CoA transferase, and hydroxyacyl CoA synthetase. These enzymes can be used with these substrates to produce in a biological system such as bacteria, yeast, fungi, or plants, polymer such as poly(3-hydroxybutyrate-co-4-hydroxyvalerate), poly(4-hydroxyvalerate), poly(3-hydroxypropionate-co-5-hydroxyvalerate), poly(2-hydroxybutyrate), poly(2-hydroxybutyrate-co-3-hydroxybutyrate), and poly(3-hydroxypropionate).

[0018] Genes encoding the required enzymes can be acquired from multiple sources. U.S. Pat. Nos. 5,798,235 and 5,534,432 to Peoples, et al., describe polyhydroxyalkanoate synthetase, reductase and thiolase. A 4-hydroxybutyryl CoA transferase gene from *C. aminobutyricum* is described by Willadsen and Buckel, FEMS Microbiol. Lett. (1990) 70: 187-192) or from *C. kluyveri* is described by Söhling and Gottschalk, 1996, J. Bacteriol. 178, 871-880). An acyl coenzyme A synthetase from *Neurospora crassa* is described by Hii and Courtright, J. Bacteriol. 1982, 150(2), 981-983. A hydroxyacyl transferase from *Clostridium* is described by Hofmeister and Bucker, Eur. J. Biochem. 1992, 206(2), 547-552.

[0019] It is important for efficient PHA production that strains do not lose the capability to synthesize the biopolymer for the duration of the inoculum train and the production run. Loss of any of the pha genes results in loss of product. Both are undesirable and stable propagation of the strain is therefore required. Merely integrating the gene encoding the transferase or synthase may not result in significant polymer production. Enzyme expression can be enhanced through alteration of the promoter region or mutagenesis or other known techniques, followed by screening for polymer production. Growth and morphology of these recombinant PHA producers is not compromised by the presence of pha genes on the chromosome.

[0020] The present invention will be further understood by reference to the following non-limiting examples.

EXAMPLE 1

Poly(3HB-co-4HV) from 4-hydroxyvalerate and glucose in *E. coli*

[0021] Construction of pFS16.

[0022] The plasmid pTrcN is a derivative of pTrc99a (Pharmacia; Uppsala, Sweden); the modification that distinguishes pTrcN is the removal of the NcoI restriction site by digestion with NcoI, treatment with T4 DNA polymerase, and self-ligation. The orfZ gene encoding the 4-hydroxybutyryl-CoA transferase from *Clostridium kluyveri* was amplified using the polymerase chain reaction (PCR) and a kit from Perkin Elmer (Foster City, Calif.) using plasmid pCK3 (Söhling and Gottschalk, 1996, J. Bacteriol. 178: 871-880) as the target DNA and the following oligonucleotide primers.

```
5'-TCCCCTAGGATTCAGGAGGTTTTTATGGAGTGGGAAGAGATATATAA

AG-3'
(orfZ 5' AvrII)

5'-CCTTAAGTCGACAAATTCTAAAATCTCTTTTTAAATTC-3'
(orfZ 3' SalI)
```

[0023] The resulting PCR product was digested with AvrII and SalI and ligated to pTrcN that had been digested with XbaI (which is compatible with AvrII) and SalI to form plasmid pFS16 such that the 4-hydroxybutyryl-CoA transferase can be expressed from the IPTG (isopropyl-β-D-glucopyranoside)-inducible trc promoter.

Construction of pFS30.

[0024] The plasmid pFS30 was derived from pFS16 by adding the *Ralstonia eutropha* PHA synthase (phaC) gene (Peoples and Sinskey, 1989, J. Biol. Chem. 264:15298-15303) which had been modified by the addition of a strong *E. coli* ribosome binding site as described by (Gerngross et. al., 1994. Biochemistry 33: 9311-9320). The plasmid pAeT414 was digested with XmaI and StuI so that the *R. eutropha* promoter and the structural phaC gene were present on one fragment. pFS16 was cut with BamHI, treated with T4 DNA polymerase to create blunt ends, then digested with XmaI. The two DNA fragments thus obtained were ligated together to form pFS30. In this construct the PHB synthase and 4-hydroxybutyryl-CoA transferase are expressed from the *A. eutrophus* phbC promoter (Peoples and Sinskey, 1989. J. Biol. Chem. 264:15298-15303). Other suitable plasmids expressing PHB synthase and 4-hydroxybutyryl-CoA transferase have been described (Hein et. al., 1997, FEMS Microbiol. Lett. 153: 411-418; Valentin and Dennis, 1997, J. Biotechnol. 58:33-38).

[0025] *E. coli* MBX769 has a PHA synthase integrated into its chromosome. This strain is capable of synthesizing poly (3-hydroxybutyrate) (PHB) From glucose with no extrachromosomal genes present. MBX769 is also deficient in fadR, the repressor of the fatty-acid-degradation pathway and effector of many other cellular functions, it is deficient in rpoS, a regulator of stationary-phase gene expression, and it is deficient in atoA, one subunit of the acetoacetyl-CoA transferase. MBX769 also expresses atoC, a positive regulator of the acetoacetate system, constitutively.

[0026] *E. coli* MBX769 carrying the plasmid pFS16 (FIG. **2**), which permitted the expression of the *Clostridium kluyveri* 4-hydroxybutyryl-CoA transferase, was precultured at 37° C. in 100 mL of LB medium containing 100 µg/mL sodium ampicillin in a 250-mL Erlenmeyer flask with shaking at 200 rpm. The cells were centrifuged at 5000 g for 10 minutes to remove them from the LB medium after 16 hours, and they were resuspended in 100 mL of a medium containing, per liter: 4.1 or 12.4 g sodium 4-hydroxyvalerate (4HV); 5 g/L sodium 4-hydroxybutyrate (4HB); 2 g glucose; 2.5 g LB broth powder (Difco; Detroit, Mich.); 50 mmol potassium phosphate, pH7; 100 µg/mL sodium ampicillin; and 0.1 mmol isopropyl-β-D-thiogalactopyranoside (IPTG). The sodium 4-hydroxyvalerate was obtained by saponification of γ-valerolactone in a solution of sodium hydroxide. The cells were incubated in this medium for 3 days with shaking at 200 rpm at 32° C. in the same flask in which they had been precultured. When 4.1 g/L sodium 4-hydroxyvalerate was present initially, the cells accumulated a polymer to 52.6% of the dry cell weight that consisted of 63.4% 3HB units and 36.6% 4HB units but no 4HV units.

[0027] When 12.4 g/L sodium 4HV was present initially, the cells accumulated a polymer to 45.9% of the dry cell weight that consisted of 95.5% 3HB units and 4.5% 4HV units but no detectable 4HB units. The identity of the PHB-co-4HV polymer was verified by nuclear magnetic resonance (NMR) analysis of the solid product obtained by chloroform extraction of whole cells followed by filtration, ethanol precipitation of the polymer from the filtrate, and washing of the polymer with water. It was also verified by gas chromatographic (GC) analysis, which was carried out as follows. Extracted polymer (1-20 mg) or lyophilized whole cells (15-50 mg) were incubated in 3 mL of a propanolysis solution consisting of 50% 1,2-dichloroethane, 40% 1-propanol, and 10% concentrated hydrochloric acid at 100° C. for 5 hours. The water-soluble components of the resulting mixture were removed by extraction with 3 mL water. The organic phase (1 µL at a split ratio of 1:50 at an overall flow rate of 2 mL/min) was analyzed on an SPB-1 fused silica capillary GC column (30 m; 0.32 mm ID; 0.25 µm film; Supelco; Bellefonte, Pa.) with the following temperature profile: 80° C., 2 min; 10 C.° per min to 250° C.; 250° C., 2 min. The standard used to test for the presence of 4HV units in the polymer was γ-valerolactone, which, like 4-hydroxyvaleric, acid, forms propyl 4-hydroxyvalerate upon propanolysis. The standard used to test for 3HB units in the polymer was PHB.

EXAMPLE 2

Poly(4HV) from 4-hydroxyvalerate in *E. coli*

[0028] *Escherichia coli* MBX1177 is not capable of synthesizing poly(3-hydroxybutyrate) (PHB) from glucose. MBX1177 is a spontaneous mutant of strain DH5□ that is able to use 4-hydroxybutyric acid as a carbon source. MBX1177 carrying the plasmid pFS30 (FIG. **2**), which permitted the expression of the *Clostridium kluyveri* 4HB-CoA transferase and the *Ralstonia eutropha* PHA synthase, was precultured at 37° C. in 100 mL of LB medium containing 100 µg/mL sodium ampicillin.

[0029] The cells were centrifuged at 5000 g for 10 minutes to remove them from the LB medium after 16 hours, and they were resuspended in 100 mL of a medium containing, per liter: 5 g sodium 4-hydroxyvalerate (4HV); 2 g glucose; 2.5 g LB broth powder; 100 mmol potassium phosphate, pH 7; 100 µg/mL sodium ampicillin; and 0.1 mmol IPTG. The cells were incubated in this medium for 3 days with shaking at 200 rpm at 30° C. in the same flask in which they had been precultured.

[0030] The cells accumulated a polymer to 0.25% of the dry cell weight that consisted of 100% 4HV units. The identity of the poly(4HV) polymer was verified by GC analysis of whole cells that had been washed with water and propanolyzed in a mixture of 50% 1,2-dichloroethane, 40% 1-propanol, and 10% concentrated hydrochloric acid at 100° C. for 5 hours, with γ-valerolactone as the standard.

EXAMPLE 3

Poly(3HB-co-2HB) from 2-hydroxybutyrate and glucose in *E. coli*

[0031] *E. coli* MBX769 carrying the plasmid pFS16 was precultured at 37° C. in 100 mL of LB medium containing 100 µg/mL sodium ampicillin in a 250-mL Erlenmeyer flask with shaking at 200 rpm. The cells were centrifuged at 5000 g for 10 minutes to remove them front the LB medium after 16 hours, and they were resuspended in 100 mL of a medium containing, per liter: 5 g sodium 2-hydroxybutyrate (2HB); 2 g glucose; 2.5 g LB broth powder; 50 mmol potassium phosphate, pH 7; 100 µg/mL sodium ampicillin; and 0.1 mmol IPTG. The cells were incubated in this medium for 3 days with shaking at 150 rpm at 33° C. in the same flask in which they had been precultured. The cells accumulated a polymer to 19.0% of the dry cell weight that consisted of 99.7% 3HB units and 0.3% 2HB units. The identity of the poly(3HB-co-2HB) polymer was verified by GC analysis of the solid product obtained by chloroform extraction of whole cells followed by filtration, ethanol precipitation of the polymer from the filtrate, and washing of the polymer with water. It was also verified by GC analysis of whole cells that had been washed with water and propanolyzed in a mixture of 50% 1,2-dichloroethane, 40% 1-propanol, and 10% concentrated hydrochloric acid at 100° C. for 5 hours, with PHB and sodium 2-hydroxybutyrate as the standards.

EXAMPLE 4

Poly(2HB) from 2-hydroxybutyrate in *E. coli*

[0032] *Escherichia coli* MBX184 is not capable of synthesizing poly(3-hydroxybutyrate) (PHB) from glucose. MBX184 is deficient in fadR and expresses atoC constitutively.

[0033] MBX184 carrying the plasmid pFS30 was precultured at 37° C. in 100 mL of LB medium containing 100 µg/mL sodium ampicillin. The cells were centrifuged at 5000 g for 10 minutes to remove them from the LB medium after 16 hours, and they were resuspended in 100 mL of a medium containing, per liter: 5 g sodium 2-hydroxybutyrate (2HB); 2 g glucose; 2.5 g LB broth powder; 50 mmol potassium phosphate, pH 7; 100 μg/mL sodium ampicillin; and 0.1 mmol IPTG. The cells were incubated in this medium for 3 days with shaking at 150 rpm at 33° C. in the same flask in which they had been precultured.

[0034] The cells accumulated a polymer to 1.0% of the dry cell weight that consisted of 100% 2HB units. The identity of the poly(2HB) polymer was verified by GC analysis of whole cells that had been washed with water and propanolyzed in a mixture of 50% 1,2-dichloroethane, 40% 1-propanol, and 10% concentrated hydrochloric acid at 100° C. for 5 hours, with sodium 2-hydroxybutyrate as the standard.

EXAMPLE 5

Poly-3HP and poly-3HP-co-5HV from 1,3-propanediol and from 1,5-pentanediol

[0035] *Escherichia coli* MBX184 carrying the plasmid pFS30 was precultured at 37° C. in 100 mL of LB medium containing 100 μg/mL sodium ampicillin. The cells were centrifuged at 5000 g for 10 minutes to remove them from the LB medium after 16 hours, and they were resuspended in 100 mL of a medium containing, per liter: 10 g 1,3-propanediol (1,3-PD) or 1,5-pentanediol (1,5-PD); 2 g glucose; 2.5 g LB broth powder; 50 mmol potassium phosphate, pH 7; 100 μg/mL sodium ampicillin; and 0.1 mmol IPTG. The cells were incubated in this medium for 3 days with shaking at 200 rpm at 30° C. In the same flask in which they had been precultured. When the diol substrate was 1,3-PD, the cells accumulated a polymer to 7.0% of the dry cell weight that consisted entirely of 3HP units. When the substrate was 1,5-PD, the cells accumulated a polymer to 22.1% of the dry cell weight that consisted of greater than 90% 3-hydroxypropionate units and less than 10% 5-hydroxyvalerate units. The identity of the poly(3-hydroxypropionate) polymer was verified by NMR analysis of the solid product obtained by sodium hypochlorite extraction of whole cells followed by centrifugation and washing of the polymer with water. The identity of both polymers was verified by GC analysis of sodium hypochlorite-extracted polymer that was propanolyzed in a mixture of 50% 1,2-dichloroethane, 40% 1-propanol, and 10% concentrated hydrochloric acid at 100° C. for 5 hours, with β-propiolactone and δ-valerolactone as the standards.

EXAMPLE 6

Poly-5HV from 5-hydroxyvaleric acid

[0036] *Escherichia coli* MBX1177 carrying the plasmid pFS30 was precultured at 37° C. in 50 mL of LB medium containing 100 μg/mL sodium ampicillin. The cells were centrifuged at 5000 g for 10 minutes to remove them from the LB medium after 8 hours, and they were resuspended in 100 mL of a medium containing, per liter: 10 g sodium 5-hydroxyvalerate (5HV); 5 g glucose; 2.5 g LB broth powder; 50 mmol potassium phosphate, pH 7; 100 μg/mL sodium ampicillin; and 0.1 mmol IPTG. The sodium 5HV was obtained by saponification of d-valerolactone. The cells were incubated in this medium for 3 days with shaking at 200 rpm at 30° C. in the same flask in which they had been precultured. GC analysis was conducted with lyophilized whole cells that were butanolyzed in a mixture of 90% 1-butanol and 10% concentrated hydrochloric acid at 110° C. for 5 hours; the standard was sodium 5-hydroxyvalerate. This analysis showed that the cells had accumulated poly(5HV) to 13.9% of the dry cell weight. The identity of the poly(5-hydroxyvalerate) polymer was verified by NMR analysis of the solid product obtained by 1,2-dichloroethane extraction of whole cells followed by centrifugation and washing of the polymer with water.

[0037] Modifications and variations are intended to come within the scope of the appended claims.

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1. A polymer produced by providing one or more substrates selected from the group consisting of 3-hydroxybutyrate, 3-hydroxypropionate, 2-hydroxybutyrate, 3-hydroxyvalerate, 4-hydroxybutyrate, 4-hydroxyvalerate, 5-hydroxyvalerate, 3-hydroxyhexanoate, 4-hydroxyhexanoate, 6-hydroxyhexanoate and other longer chain 3-hydroxyacids containing seven or more carbons,

wherein the biological system expresses enzymes selected from the group consisting polyhydroxyalkanoate synthase, acyl-CoA transferase, hydroxyacyl CoA transferase, and hydroxyacyl CoA synthetase such that the polymers accumulate.

2. The polymer of claim **1** selected from the group consisting of poly(3-hydroxybutyrate-co-4-hydroxyvalerate), poly (4-hydroxyvalerate), poly(3-hydroxypropionate-co-5-hydroxyvalerate), poly(2-hydroxybutyrate), poly(2-hydroxybutyrate-co-3-hydroxybutyrate), poly(3-hydroxypropionate), produced in a biological system selected from the group comprising bacteria, yeasts, fungi and plants, wherein the biological system expresses enzymes selected from the group consisting polyhydroxyalkanoate synthase, acyl-CoA transferase and hydroxyacyl CoA transferase, and hydroxyacyl CoA synthetase such that the polymers accumulate in the presence of appropriate substrates.

3. The polymer of claim **1** wherein the polymer is poly(3-hydroxybutyrate-co-4-hydroxyvalerate).

4. The polymer of claim **1** wherein the polymer is poly(4-hydroxyvalerate).

5. The polymer of claim **1** wherein the polymer is poly(3-hydroxypropionate-co-5-hydroxyvalerate).

6. The polymer of claim **1** wherein the polymer is poly(3-hydroxypropionate).

7. A polyhydroxyalkanoate polymer comprising 2-hydroxybutyrate as a comonomer, wherein the polymer is produced in a biological system selected from the group comprising bacteria, yeasts, fungi and plants, wherein the biological system expresses enzymes selected from the group consisting polyhydroxyalkanoate synthase, acyl-CoA transferase, hydroxyacyl CoA transferase, and hydroxyacyl CoA synthetase such that the polymers accumulate in the presence of appropriate substrates.

8. The polymer of claim **7** wherein the polymer is poly(2-hydroxybutyrate).

9. The polymer of claim **7** wherein the polymer is poly(2-hydroxybutyrate-co-3-hydroxybutyrate).

10. (canceled)

11. (canceled)

12. (canceled)

* * * * *

ROCKWOOD PIGMENTS
Colors • Systems • Solutions

MATERIAL SAFETY DATA SHEET

MSDS CODE:	CB1	Page 1 of 5
Date Revised:	05/18/2010	
Prepared By:	Nick Paris	Reason for Revision: See Section 16

1. CHEMICAL, PRODUCT AND COMPANY IDENTIFICATION:

Product Code(s):	**8405, C391, C351, CARBOFIN®**
Product Name:	Carbon Black pigment
Chemical Family:	Carbon
Synonyms:	Wettable Carbon Black pigment, Lampblack
C.A.S. Number:	1333-86-4
Color Index Name:	Pigment Black 7
Color Index Number:	77266

Supplier's Name/Address:
Rockwood Pigments/Davis Colors, 7011 Muirkirk Road, Beltsville, Maryland, USA 20705
Business Tel: (301) 210-7800 9a-5p (0900-1700) EST M-F
Rockwood Pigments/Davis Colors, 3700 East Olympic Boulevard, Los Angeles, California, USA 90023
Business Tel: (323) 269-7311 9am-5pm (0900-1700) PST M-F

24 Hour Emergency (Chemtrec): 800-424-9300

2. COMPOSITION/INFORMATION ON INGREDIENTS

OSHA Hazardous Ingredients (29CFR1910.1200):

			Exposure Limits (8 Hrs.TWA)	
Components:	C.A.S.	%	OSHA PEL	ACGIH TLV
Carbon Black pigment	1333-86-4	(90+)	3.5 mg/m^3	3.5 mg/m^3

Non-Hazardous Ingredients:

			Exposure Limits (8 Hrs.TWA)	
Components:	C.A.S.	%	OSHA PEL	ACGIH TLV

3. HAZARDS IDENTIFICATION

*********************************** EMERGENCY OVERVIEW ***********************************

Solid black powder with little to no odor. Inhalation can cause temporary lung irritation. May ignite in air above 500°F. Will burn in fire. Carbon monoxide and carbon dioxide are emitted. It may not be obvious that product is burning unless it is stirred and sparks are apparent. Packaging material can burn or melt in fire, producing toxic smoke and fumes.

****

HMIS Codes: H=0, F=1, R=0, P=0 (0=Minimal, 1=Slight, 2=Moderate, 3=Serious, 4=Severe)

Potential Health Effects:

Eyes:	Non-irritating to the eyes. Excessive exposure to airborne dust may reduce visibility and/or cause unpleasant deposits.
Skin:	Will not irritate skin and is not likely to cause allergic skin reaction. Irritation to skin or mucous membranes can occur by direct mechanical action or by rigorous skin cleaning necessary for removal of dust.
Ingestion:	Small amounts (a tablespoonful) swallowed are not likely to cause injury. No hazard in normal industrial use.
Inhalation:	Not a hazard in normal industrial use. As with all dusty materials, inhalation may cause respiratory irritation, sneezing, coughing, and runny nose.

Human Effects and symptoms of overexposure:

Acute:	Dust concentrations above the permissible exposure limit may cause temporary upper respiratory tract discomfort.
Chronic:	Epidemiological studies of workers in the Carbon Black pigment producing industries of North America and Western Europe show no significant adverse health effect due to occupational exposure to Carbon Black pigment. Early studies in the former USSR and Eastern Europe report respiratory diseases among workers exposed to Carbon Black pigment, including bronchitis, pneumonia, emphysema, and rhinitis. Such studies are of questionable validity, due to inadequate study design and methodology, lack of appropriate controls for cigarette smoking, and other confounding factors such as concurrent exposures to carbon monoxide, coal oil and petroleum vapors. Moreover, review of these studies indicates that concentrations of Carbon Black pigment were greater than current occupational exposure standards. In Monograph 65, issued in April 1996, the International Agency for Research on Cancer (IARC) re-evaluated Carbon Black pigment and concluded that: "Although one cohort study on the Carbon Black pigment production industry showed slight excesses of cancer, the totality of the

	epidemiology studies, both in the Carbon Black pigment production industry and in some user industries, suggested that there is inadequate evidence for the carcinogenicity in humans of Carbon Black pigment."
Other Effects:	None known.
Medical Conditions Aggravated by Exposure:	None known. Carbon Black pigment, like any nuisance dust, may aggravate certain pre-existing upper respiratory disorders, such as bronchitis or asthma.
Carcinogenicity:	IARC: Listed Group 2B/Possible Human Carcinogen NTP: Not Listed OSHA: Not Listed
Other:	The IARC changed the listing of Carbon Black pigment April 12, 1996 from Category 3 (insufficient evidence to make a determination) to Category 2B (Known animal carcinogen/possible human carcinogen) based on the results of rat inhalation studies of Carbon Black pigment, despite the lack of any parallel evidence in humans or other animal species. See section 11.

4. FIRST AID MEASURES

Eyes:	Flush eyes with water, lifting eyelids periodically. Remove contact lenses. Continue flushing for 15 minutes or until eyes return to normal. Get medical attention if irritation develops or persists.
Skin:	Wash with soap and water. Get medical attention if irritation develops or persists. Wash clothing before re-use.
Ingestion:	Swallowing less than an ounce (less than 30 grams) will not cause harm. For larger amounts, do not induce vomiting, but give one or two glasses of water to drink and Contact medical personnel or poison control center immediately. Do not give anything by mouth to an unconscious person.
Inhalation:	Move from dusty area to fresh air and get medical attention for any breathing difficulty. If breathing is difficult, give oxygen. If not breathing, give artificial respiration. Get immediate medical attention.

5. FIRE FIGHTING MEASURES

Flammable Properties:	Not Flammable.
Flash Point:	May ignite in air above 315C. Flash point is above 500°C.
Upper Explosive Limit (UEL):	122 g/m3
Lower Explosive Limit (LEL):	Will not explode
Auto-ignition Temperature:	Exposure to excessive heat greater than 500°F (260°C) can cause this product to ignite.
Extinguishing Media:	Use water fog or foam to cool below ignition point. Wets poorly with water or water spray. Use extinguishing agents that are suitable to the surrounding fire;water spray, dry chemical, foam or CO_2
Fire fighting Instructions:	This product may contain residual oxygenated volatiles that can further react and generate heat. In the event the product reaches 230 F, bags should be separated by an air space and allowed to cool and should be removed from the vicinity of other combustibles. Carbon monoxide and carbon dioxide are emitted. It may not be apparent when Carbon Black pigment is burning until it is stirred and sparks are visible. Firefighters should be equipped with self-contained breathing apparatus to protect against potentially toxic and irritating fumes and smoke inhalation.

6. ACCIDENTAL RELEASE MEASURES

Small Spill:	If dust is generated, use appropriate respiratory protection. Vacuum or scoop material into an appropriately marked container for re-use or disposal. Avoid excessive generation of dust.
Large Spill:	Use recommended protective clothing and respiratory protection. Use shovel to reclaim material. Vacuum or scoop material into an appropriately marked container for re-use or disposal. Avoid excessive generation of dust. Spill area can be washed with water. Collect wash water for approved disposal. Prevent runoff from entering storm sewers and ditches which lead to natural waterways.

7. HANDLING AND STORAGE

Storage:	Store dry at ambient temperature away from food and beverages, excessive heat or flame sources (furnace, kilns, boilers etc.). Avoid breathing dust. Avoid contact with eyes and skin. Wash thoroughly after handling.
Handling:	Avoid breathing dust. Avoid getting in eyes or on skin. Wash thoroughly after handling. Avoid contact with moisture. Re-seal bag immediately after use. Pallets are wrapped in polyethylene plastic. Removal may cause an electrostatic spark; therefore removal of the wrap should not be in the presence of flammable vapors.

Storage Temperature (Min/Max) :	Ambient/50°C (122°F)
Shelf Life :	Unlimited in closed container
Special Sensitivity :	Excessive Heat and Strong oxidizing agents. such as chlorates, bromates, and nitrates.
Other Precautions :	None

MATERIAL SAFETY DATA SHEET

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering Controls:	Maintain air levels below the recommended exposure limit using exhaust ventilation if necessary.
Eyes:	Safety Glasses.
Skin:	Body-covering clothing. Rubber, Plastic, Leather or cloth gloves are suggested to facilitate personal hygiene.
Respiratory Protection:	Workplace ambient dust concentrations should be monitored and if the recommended exposure limit is exceeded, a NIOSH/MSHA approved respirator with dust prefilter should be worn.
Other:	Emergency showers and eye wash stations should be available. Educate and train employees in the safe use and handling of hazardous chemicals.
Work/Hygiene Practices:	Employees should wash their hands and face before eating, drinking or using tobacco products.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance	Solid Black Powder
Odor	Odorless
Physical State	Dry Powder
pH	7 - 9 in 50 gr/l H_2O aqueous suspension; DIN 787/9
Vapor Pressure	Not a vapor
Vapor Density	Not a vapor
Boiling Point	Not applicable
Freezing Point	Not applicable
Melting Point	Greater than 500°F (260°C)
Solubility in Water	Insoluble
Specific Gravity (g/ml)	1.6 to 1.9 @ 20°C (68°F); DIN 787/10
Bulk Density (kg/m^3)	Not available
Particle Size (microns)	0.03-0.10
Volatile Organic Compounds (VOC)	None
Chemical Formula	C

10. STABILITY AND REACTIVITY

Chemical Stability (Conditions to Avoid):	Stable. Keep away from flames and heat. Exposure to excessive heat greater than 500°F (260°C) can cause this product to ignite.
Incompatibility (materials to avoid):	Excessive heat and Strong oxidizing agents. such as chlorates, bromates, and nitrates.
Decomposition Temperature F° (C°):	Does not decompose
Hazardous Decomposition Products:	Carbon monoxide and carbon dioxide when burning.
Hazardous Polymerization:	Will not occur

11. TOXICOLOGICAL INFORMATION

Eyes:	Not irritating to rabbit eyes
Skin:	Not irritating to rabbit skin Dermal, LD 50 greater than 240mg/kg, IP injection, mice and rats
Ingestion:	Non irritating. The oral, LD50 for rats is greater than 5000 mg/l
Inhalation:	Non irritating. LC 50 greater than 156 mg/m^3, mice and rats
Subchronic:	Data not established for product
Chronic/Carcinogenicity:	Data not established for product
Other (Mutagenic, Teratogenic, Reproductive Tests):	This product contains less than 0.1% of absorbed PAHs (polynuclear aromatic hydrocarbons).In non-absorbed form, som PAHs have been found to be carcinogens in animal studies. No correlating carcinogenic effect, however, has been observed in humans due to exposure to Carbon Black pigment. Chronic inflammation, lung fibrosis and lung tumors have been observed in some rats experimentally exposed, for long periods of time, to very high concentrations of Carbon Black pigment and several other insoluble fine dust particles. Tumors have not been observed in other animal speicies (i.e mouse and hamster) under similar circumstances and study condidions. Researchers conducting the rat inhalation studies believe that these effects most likely result from the massive accumulation of small dust particles in the lung which overwhelm the natural lung clearance mechanism, known as the "lung overload" phenomenon, rather than from a

specific chemical effect of the dust particles in the lung.

12. ECOLOGICAL INFORMATION

Ecotoxicological Information:	Fish toxicity: Golden Orfe (Leuciscus idus) LCo greater than 1000 mg/l
Chemical Fate Information:	No appreciable bioconcentration is expected in the environment or biological organisms. Does not biodegrade. Not mobile in soil. Not soluble in water.

13. DISPOSAL CONSIDERATIONS

Material which cannot be re-used should be disposed in accordance with federal, state and local environmental control regulations at an authorized site. This product when discarded as sold is not a RCRA hazardous waste. However, under RCRA, it is the responsibility of the product user to determine at the time of disposal, whether a material containing the product or derived from the product should be classified as a hazardous waste. (40CFR 261.20-24)

14. TRANSPORT INFORMATION

DOT Shipping Name	Carbon Black pigment
Technical Shipping Name	Pigment, NOI
DOT Hazardous Classification	Non-Regulated
DOT Hazard Class	Non-Regulated
DOT Identification Number	None
DOT Labels required	None
DOT Placards required	None
UN Class	Combustible solid
UN/NA Number	None
Freight Class	45
Harmonized Tariff Number	2803.00.00.0010

15. REGULATORY INFORMATION

********************************** U.S. Federal Regulations **********************************

OSHA:	This product is considered Hazardous by definition of Hazard Communication Standard (29 CFR 1910.1200).
CERCLA/SUPERFUND:	(40 CFR 117,302) Reportable Quantity (RQ): Not Reportable, however, we recommend you contact local authorities to verify requirements for your site.

Superfund Amendments and Reauthorization Act (SARA), Title III:

Section 302 (Extremely Hazardous Substances):	None
Section 311/312 (Hazard Categories):	Reportable on Tier I and/or Tier II reports if present at a facility at any on time in amounts equal to or greater than 10,000 pounds.

Section 313 (Reportable Toxic Ingredients):

Chemical Name:	C.A.S.	Concentration
None Reportable		

T.S.C.A.:	This product is listed on TSCA Inventory. Carbon black pigment is a Chemical Hazard Information Profile (CHIP) Chemical under TSCA.
CONEG:	This product meets the Coalition of Northeast Governors (CONEG) Source Reduction Council limits for the sum of the levels of Lead, Cadmium, Mercury and Hexavalent Chromium of less than 100 parts per million by weight.
U.S. Clean Air Act, 1990:	Carbon Black pigment is not made with nor does it contain any Class 1 or Class 2 ozone depleting substances as defined under the 1990 amendments to the act.
U.S. FDA Regulations:	Carbon Black pigment is permitted for indirect contact with food and drugs when used as a filler in rubber articles intended for repeat use under 21 CFR (Code of Federal Regulations) 177.2600. Limitation: Total Carbon Black pigment in the rubber may not exceed 50% by weight of the rubber product. This product, which is a furnace process black, may not exceed 10% by weight of rubber product intended for use in contact with milk or edible oils.
U.S. NSF Certification:	Information on Carbon Black pigments has been given to the National Sanitation Foundation (NSF) and may be used to obtain approval for formulations using Carbon Black pigment.

********************************** International Regulations **********************************

Australia:	Australian Inventory of Chemical Substances (AICS)
Canadian WHMIS:	Not restricted/non-hazardous, controlled substance (D2A)
Canadian Environmental Protection Act (CEPA):	All components of this product are on the Domestic Substances List (DSL), and acceptable for use under the provisions of CEPA.
Europe (EU):	All components of this product are on the European Inventory of Existing Commercial Chemical Substances (EINECS).
Japan:	Ministry of International Trade & Industry List of Existing Chemical Substance (MITI)
Korea:	Toxic Chemical Control Law (TCCL)

********************************** State Regulations **********************************

CA =
MA =
NJ4 =
PA3 =

Louisiana: Right to know legislation requires inventory reporting through Community Right-to-Know when the quantity of Carbon Black pigment exceeds 500 pounds on any given day. Spills or releases beyond the site of the facility of greater than 5,000 pounds are required to be immediately reported to the state Emergency Response Commission via the Office of the State Police, Transportation and Environmental Safety Section, Hazardous Material Hotline, (504) 925-6596 (collect calls accepted 24 hours per day).

Chemical Name:	C.A.S.	Concentration	State Code
Carbon Black pigment	1333-86-4	90-100%	NJ4

Note: This information based on random sample analyses. Actual content may vary from batch to batch.

16. OTHER INFORMATION

Reason for revision:		
	7/23/2003	- revised to reflect OSHA hazardous status.
	1/11/2006	- Update review date.
	3/8/2006	- Added Harmonized Tariff Number to section 14.
	5/18/2010	- Update review date.

HMIS Codes: H=0, F=1, R=0, P=0 (0=Minimal, 1=Slight, 2=Moderate, 3=Serious, 4=Severe)

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

DATE: November 22, 2005

ACTION MEMORANDUM

SUBJECT: Inert Reassessment – Carbon Black, CAS Reg. No. 1333-86-4

FROM: Pauline Wagner, Chief Pauline Wagner 11/22/05
Inert Ingredient Assessment Branch

TO: Lois A. Rossi, Director
Registration Division

I. FQPA REASSESSMENT ACTION

Action: Reassessment of one inert exemption from the requirement of a tolerance.

Chemical: Carbon Black
CFR: 40 CFR part 180.930 [formerly 40 CFR180.1001(e)]
CAS Reg. No: 1333-86-4

Use Summary: The major use of carbon black is in the manufacture of rubber products, particularly in tires and other automotive components. Carbon black is also used as a pigment or colorant in inks, paints, leather dyes, ceramics, and coatings; as well as in plastics. It is also has limited use as an inert ingredient in pesticide products as a colorant/pigment in animal ear-tag.

List Reclassification Determination: Based on the low risk finding, this inert ingredient can be reclassified from List 3 to 4B.

II. MANAGEMENT CONCURRENCE

I concur with the reassessment of one exemption from the requirement of a tolerance for the inert ingredient carbon black CAS Reg. No. 1333-86-4, and with the

List reclassification determination(s), as described above. I consider one exemption established in 40 CFR part 180.930 [formerly 40 CFR180.1001©] to be reassessed for purposes of FFDCA's section 408(q) as of the date of my signature, below. A Federal Register Notice regarding this tolerance exemption reassessment decision will be published in the near future.

Donald R Stubbs

Lois A. Rossi, Director
Registration Division

Date: 11/22/05

CC: Debbie Edwards, SRRD
Joe Nevola, SRRD

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF PREVENTION,
PESTICIDES, AND TOXIC
SUBSTANCES

November 21, 2005

MEMORANDUM

SUBJECT: Reassessment of one Exemption from the Requirement of a Tolerance for Carbon Black

FROM: Bipin Gandhi
Inert Ingredient Assessment Branch (IIAB)
Registration Division (7505C)

TO: Pauline Wagner, Chief
Inert Ingredient Assessment Branch (IIAB)
Registration Division (7505C)

Background

Attached is the science assessment for carbon black. Carbon black has one exemption from the requirement of a tolerance under 40 CFR §180.930 as pigment/colorant in animal tags as listed in Table 1 under use information. This assessment summarizes available information on the use, physical/chemical properties, toxicological effects, exposure profile, environmental fate, and ecotoxicity of carbon black. The purpose of this document is to reassess the existing exemption from the requirement of a tolerance for residues of carbon black when used as an inert ingredient in pesticide formulations as required under the Food Quality Protection Act (FQPA).

Executive Summary

The only use for which carbon black is approved as an inert ingredient in pesticide formulations under 40 CFR 180.930 as colorant/pigment in animal ear-tag. All the toxicity studies reported in the literature and discussed below are for carbon black particles and not relevant to its use as colorant/pigment in (plastic) animal tag. Therefore, the toxicity is low, the exposure is low and so the risk is low. There is no expected residues of concern in food, water, or residential exposure. In summary, the aggregate exposure is low. There is a safe history of carbon black when used in tires, plastics, automobile components, inks, adhesives, paints, dyes and ceramics.

Taking into consideration all available information on carbon black, EPA has determined that there is a reasonable certainty that no harm to any population subgroup will result from aggregate exposure to carbon black when used as inert ingredient in pesticide formulations when considering the dietary exposure and all other non-occupational sources of pesticide exposure for which there is reliable information. Therefore, it is recommended that one exemption from the requirement of a tolerance established for residues of carbon black be maintained and considered reassessed as safe under section 408(q) of the FFDCA.

I. Introduction

This report provides a qualitative assessment for carbon black, a pesticide inert ingredient in pesticide formulations when used as colorant/pigment in animal tags. This chemical has an exemption from the requirement of a tolerance under 40 CFR §180.930.

Carbon blacks are commercially produced by the partial combustion or thermal decomposition of gaseous or liquid hydrocarbons. Depending on the manufacturing process used, industrial carbon blacks are known as acetylene black, channel black, lamp black, furnace black, or thermal black. Other synonyms include Pigment Black 7, Pigment Black 6, impingement black, gas-furnace black, oil-furnace black, or therma-atomic black (BIBRA, 1990; IARC, 1996). Food grade carbon blacks are produced by the carbonization of plant materials such as peat, and are known as "vegetable blacks." Modern carbon blacks are largely (>90%) furnace blacks (IARC, 1996). The various carbon blacks exhibit a range of particle sizes and differences in degree of particle aggregation, but are similar in that they all possess low ash content and high surface area/unit mass (IARC, 1996).

II. Use Information

A. Pesticide Uses

At present, carbon black is exempted from tolerance requirements in pesticide formulations applied to animals when used as colorant/pigment in animal tags (40CFR §180.930) as shown table 1 below.

Table 1. Pesticide Uses

CFR Citation				CAS Reg. No. /Name
40 CFR §	**Inert Ingredients**	**Limits**	**Uses**	
180.930*	Carbon Black	(none)	Colorant/ Pigment in animal tag	1333-86-4 Carbon Black

*Residues listed in 40 CFR §180.930 are exempt from the requirement of a tolerance when used in accordance with good agricultural practice as inert (or occasionally active) ingredients in pesticide formulations applied to animals.

B. Other Uses

The other uses include indirect contact with food (as adhesive component, as colorant in coatings, etc.) is permitted (21 CFR 175.105; 177.1650; 177.2400; 177.2410). Carbon black manufactured by the channel process cannot be directly used in food, drugs or cosmetics (21 CFR 81.10). In 1993, worldwide production of carbon black approximated 6 million tons (IARC, 1996).

The major use of carbon black is as a reinforcing and abrasion-resistant material in the manufacture of rubber products, particularly in tires and other automotive components. Carbon black is also used as a pigment or colorant in inks, paints, leather dyes, ceramics, and coatings; as well as in plastics (to which it imparts weathering resistance, electrical conductivity, and antistatic properties) (IARC, 1996).

III. Physical and Chemical Properties

Table 2. Physical and Chemical Properties[1]

Parameter	Value
Structure	C
Molecular formula	C
Physical Form/color	Finely divided black solid particles; elemental amorphous carbon powder
Odor	Odorless
Density	1.8 – 2.1
pH	3 – 9.5 (depending on manufacturing process)
Molecular Wt.	12
Melting Point	3550° C
Boiling Point	4827 ° C
Sublimation Point	3367 ° C
Solubility	Insoluble in all commercial solvents; insoluble in water
Vapor Pressure	negligible
Vapor Density	NA
Henry's Law Constant	NA
Dissociation constants	NA
Log K_{ow}	NA
Average Particle Diameter	17 – 500 mm (depending on manufacturing process)
Surface Area	6 – 200 m^2/g

1 IARC, 1996

IV. Hazard Assessment

Carbon black is not expected to pose a hazard when used in ear tags. Much of the toxicity data on carbon black has been generated via the inhalation route due to concerns over adverse effects on the respiratory tract. These data show that high levels of particulate carbon cause respiratory damage via a mechanism known as "lung overload". Oral ingestion of carbon has not been shown to cause adverse effects even at doses of one gram or greater over a two year period. As a solid, carbon black is not expected to be absorbed through the skin

A. Hazard Profile

The information for this profile was derived from studies identified in searches of major bibliographic data bases, and reliable secondary references. A very large body of data on carbon black toxicity exists in the literature. Therefore, toxicity information for carbon black presented here is primarily from reviews published by IARC (1996), BIBRA International Ltd (1990), WHO (1988), NCI (1985),IPCS (2001) and RTECS (2004).

Because these documents have undergone several levels of technical review, it is assumed for the purposes of the present report that any referenced toxicity data cited within them are also reliable.

B. Toxicological Data

Acute Toxicity: The literature contains very little information on the acute or short-term toxicity of carbon black, and considers carbon black to be a non-specific respiratory irritant and nuisance dust as free particles). In general, data indicate that acute effects of carbon black exposures are the same as those observed for other insoluble particulates. As a consequence, the bulk of the toxicity studies for this material have been designed to determine tumorigenicity after long-term exposure, or after a lengthy latency period following exposure to overload concentrations.

The few acute experimental studies available indicate low mammalian toxicity: rat oral LD_{50} >15,400 mg/kg, rabbit dermal LD_{50} >3000 mg/kg (ATDAE1, as cited in RTECS).

Numerous intratracheal instillation exposures to mice and rats indicate that high acute doses elicit a specific inflammatory response which is thought to be related to the large surface area presented by the instilled carbon black particles (Bowden and Adamson, 1978, 1982; Adamson and Bowden, 1978, 1980, 1982a, b; all as cited in IARC, 1996). Similar findings were noted for inhalation exposures in rats.

Subchronic/Chronic toxicity. Subchronic and chronic inhalation exposure studies have been performed in rats and mice for a range of concentrations (1.1-52.8 mg/m^3) and exposure durations (multiple hours/day at 5 days/wk for 13 wks-24 months) (Heinrich et al., Dungworth et al., Nolte et al.1994, Driscoll et al.; all as cited in IARC 1996). IARC (1996) considers that the body of evidence contained in these studies indicate that "once a certain lung burden has been achieved, inhalation of carbon black in rats results in significant [pulmonary] inflammatory responses." This study was based on free particles.

RTECS posts a 90-day intermittent inhalation "lowest published toxic concentration" of 50 mg/m^3 for 6 hr/day (TOXID9, as cited in RTECS) for respiratory tract changes in the rat, and an intermittent 4-week dermal "lowest published toxic dose" of 11 g/kg for weight loss or decreased weight gain in the rat (as free particles) (NTIS OTS0534753, as cited in RTECS).

Long-term dietary studies of laboratory rodents fed large concentrations of carbon black in the diet (free particles)(e g., 1 g/g body wt/yr; approximately 2 g/kg feed) did not provide any indication of pathological effects in rodent GI tracts (Buddingh et al., Pence and Buddingh, 1985, 1987; all as cited in IARC, 1996). Other studies indicate that carbon black is relatively innocuous by the ingestion route (Nau et al., 1976, and Steiner; both as cited in IARC, 1996; Von Hamm et al., as cited in Robertson and Smith).

Developmental Toxicity No developmental studies with the free or bound carbon black were identified, but no effects on reproductive organs of either male or female rats were reported in long term studies.

Mutagenicity. Assays have been performed on multiple commercial carbon blacks, as well as organic extracts of several. IARC (1996) has determined that "most assays for mutagenicity are negative for carbon black

Carcinogenicity. Carbon black has been evaluated for carcinogenicity by a number of IARC Working Groups (1984, 1987, 1996). Since occupational exposure levels in the carbon black production industry have historically been high, workers in this industry have been the subject of many epidemiological studies. Nine such studies of workers in the US, UK, Sweden and Canada were examined in detail by IARC (1996), which "considered the whole body of evidence rather weak and the results conflicting."

The majority of carcinogenicity studies of carbon black are by the inhalation route. These studies have shown conflicting results. One study in female mice was negative for respiratory track tumors, while two other studies using both male and female rats also showed benign and malignant tumors in the females. The particle size and form may impact the toxicity of the respiratory system.

Nau et al. (as cited in IARC, 1996) determined that repeated and prolonged painting of various carbon black suspensions onto the skin of mice demonstrated no dermal carcinogenic effect. However, tumors (some in other organs) resulted if benzene extracts of the same carbon blacks were applied to the skin of mice.

Some recent reviews point out that current evaluations of carbon black carcinogenicity are heavily dependent upon the results of rat exposure studies, and may thus not be fully applicable to the response of human lung tissue under similar exposure conditions (Brockmann et al., 1998; Levy, 1996). Brockmann et al. (1998) and Levy (1996) recommend improvements in cancer study design and techniques, and greater precision in the nomenclature used to describe observed neoplastic lesions.

D. Special Consideration for Infants and Children

Carbon black has low subchronic and chronic toxicities. Although no developmental or reproductive studies, *per se*, were identified, long term studies have not demonstrated any effects on the reproductive organs of male or female rats. Additionally, the poor to nil absorption of carbon black as demonstrated by the lack of significant adverse effects by the oral route even at high doses would mitigate any concerns. Carbon black is used in small amounts in insecticidal animal ear tags that are firmly attached to the animals. The chemical is expected to remain incorporated in the ear tag and not disperse onto the animal during movement. In the worse-case scenario, residues from use of the ear tags are expected to be in micrograms per kilogram of animal weight (through the licking of the ear tags by other animals). Dietary exposure to carbon black in meats and meat products is expected to be several orders of magnitude less than levels in the animal, therefore, far below levels of concern. Based on the available exposure and toxicity information, safe history of similar uses, a safety factor analysis has not been used to assess the risks resulting from the inert pesticidal use of carbon black, and therefore, an additional tenfold safety factor for the protection of infants and children is unnecessary.

V. Environmental Fate Characterization/Drinking Water Considerations

Carbon black can be released into the environment from various industrial sources. However, the release from the pesticidal uses are negligible because its use is limited to composition of pigments and dyes and as a component of plastic ear tags for animals. It is not soluble in water or any other commercial solvents. Carbon black is not subject to degradation per se because it is not expected to photolyze, hydrolyze, or subject to metabolic degradation. It will not enter into the environment because it is incorporated into plastic ear tags and plastics in general do not degrade. It is an inert material and does not harm water or the environment. It is adsorb to the soil and does not harm soil or the crops grown on such soils.

Based on all of the above information and the physical/chemical properties of carbon black, concentrations of this chemical in drinking water (from runoff), are not expected from their use as colorant/pigment in animal tags in pesticide products.

Exposure Assessment

The only pesticide inert ingredient use of carbon black is as pigment in animal tag. Animal ear tags are small in size (9.5 to 14.5 g), and the amount of inert ingredient that is used as pigment in animal tag is small compare to total weight of the tag. Residential exposures (inhalation and dermal) to carbon black are not expected to occur because the carbon black as pigment which is incorporated into animal ear tags that are firmly attached to the animal. For the same reason, dietary exposures (food and drinking water) to this chemical are unlikely and there are no other food or feed crop uses for this chemical. In a worst case scenario, maximum exposure to carbon black would be in micrograms per kilogram of animal, which is well below levels of concern. Wildlife exposure and exposure to aquatic organism will be much less because of the incorporation of carbon black into plastic animal ear tag. In addition, carbon black is innocuous in nature, so no harm is expected from its use as pigment in animal ear tag.

Aggregate Exposure

In examining aggregate exposure, FFDCA section 408 directs EPA to consider available information concerning exposures from the pesticide residue in food and all other non-occupational exposures, including drinking water from ground water or surface water and exposure through pesticide use in garden, lawns, or buildings (residential and other indoor uses). As stated above under 'Exposure Assessment' there will not be any exposure through food, water or residential uses.

Cumulative Exposure

Section 408(b)(2)(D)(v) of the FFDCA requires that, when considering whether to establish, modify, or revoke a tolerance, the Agency consider "available information" concerning the cumulative effects of a particular pesticide's residues and "other substances that have a common mechanism of toxicity."

Unlike other pesticides for which EPA has followed a cumulative risk approach based on a common mechanism or toxicity, EPA has not made a common mechanism of toxicity safety finding as to carbon black, and any other substances, and carbon black do not appear to produce toxic metabolites produced by other substances. For the purpose of these tolerance actions, therefore, EPA has not assumed that carbon black has a common mechanism of toxicity with other substances. For information regarding EPA's efforts to determine which chemicals have a common mechanism of toxicity and to evaluate the cumulative effects of such chemicals, see the policy statements released by EPA's Office of Pesticide Programs concerning common mechanism determinations and procedures for cumulating effects from substances found to have a common mechanism on EPA's website at http://www.epa.gov/pesticides/cumulative/.

IX. Human Health Risk Characterization

The only use for which carbon black is approved as an inert ingredient in pesticide formulations is under 40 CFR 180.930 as colorant/pigment in animal ear-tag. The majority of toxicity studies reported in the literature and discussed above are inhalation studies for carbon black particles and are not relevant to its use as colorant/pigment in (plastic) animal tag. One long term oral study in rats did not produce any adverse effects at doses of 1000 mg/kg. Therefore, the toxicity is low, the exposure is low and so the risk is low. There are no expected residues of concern in food, water, or residential exposure. There is a safe history of carbon black when used in tires, plastics, automobile components, inks, adhesives, paints, dyes and ceramics.

Taking into consideration all available information on carbon black, EPA has determined that there is a reasonable certainty that no harm to any population subgroup will result from aggregate exposure to carbon black when used as inert ingredient in pesticide formulations when considering the dietary exposure and all other non-occupational sources of pesticide exposure for which there is reliable information. Therefore, it is recommended that the one exemption from the requirement of a tolerance established for residues of carbon black be maintained and considered reassessed as safe under section 408(q) of the FFDCA.

X. Ecotoxicity and Ecological Risk Characterization

Carbon is not soluble in water or any commercially available solvents and it is innocuous in nature, therefore, no ecological risk is expected. Following are the ecosar predicted calculations in table 3.

Table 3. Ecosar predicted data

Organism	Duration	End Pt	Predicted mg/L (ppm)
Fish	14-day	LC50	248.833
Fish	96-hr	LC50	166.759
Daphnid	48-hr	LC50	164.244
Green Algae	96-hr	EC50	95.717
Fish	30-day	Chv	17.648
Daphnid	16-day	EC50	4.940

Green Algae	96-hr	Chv	4.729
Fish	96-hr	LC50	21.718
Mysid Shrimp	96-hr	LC50	114.892
Earthworm	14-day	LC50	234.892 (dry wt soil)

* ECOSAR Run

XI. References:

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Material Safety Data Sheet
Titanium(IV) oxide

MSDS# 23510

Section 1 - Chemical Product and Company Identification

MSDS Name:	Titanium(IV) oxide
Catalog Numbers:	AC194340000, AC194340010, AC194340050, AC194340250, AC213580000, AC213580010 AC213580010, AC213580050, AC213581000, AC270460000, AC270460010, AC270461000 AC270461000, AC270465000, AC277370000, AC277370010, AC277370100, AC384290000 AC384290000, AC384290010, AC384290500, AC384292500, NC9803595, T315-500
Synonyms:	Anatase; Titania; Titanic anhydride; C.I. 77891; Rutile.

Company Identification:	Fisher Scientific One Reagent Lane Fair Lawn, NJ 07410
For information in the US, call:	201-796-7100
Emergency Number US:	201-796-7100
CHEMTREC Phone Number, US:	800-424-9300

Section 2 - Composition, Information on Ingredients

CAS#:	13463-67-7
Chemical Name:	Titanium dioxide
%:	>98
EINECS#:	236-675-5

Hazard Symbols: XN

Risk Phrases: 40

Section 3 - Hazards Identification

EMERGENCY OVERVIEW

Warning! May cause eye, skin, and respiratory tract irritation. Possible cancer hazard. May cause cancer based on animal data. Target Organs: Respiratory system.

Potential Health Effects

Eye:	Dust may cause mechanical irritation.
Skin:	Dust may cause mechanical irritation. Low hazard for usual industrial handling. Skin absorption not likely.
Ingestion:	No hazard expected in normal industrial use. Ingestion of large amounts may cause pain, constipation or diarrhea. May cause ataxia (failure of muscular coordination), increased blood pressure, hallucinations, hypermotility, muscle contraction/spasticity, fatigue, psychosis, and tremors.
Inhalation:	Dust is irritating to the respiratory tract. May be harmful if inhaled. May cause pulmonary fibrosis and permanent damage.
Chronic:	May cause cancer according to animal studies. Chronic inhalation may cause pulmonary fibrosis. Prolonged or repeated exposure may cause lung irritation, chest pain, and pulmonary edema.

Section 4 - First Aid Measures

Eyes:	Immediately flush eyes with plenty of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Get medical aid.

Skin: Get medical aid if irritation develops or persists. Wash clothing before reuse. Flush skin with plenty of soap and water.

Ingestion: Do not induce vomiting. If victim is conscious and alert, give 2-4 cupfuls of milk or water. Get medical aid.

Inhalation: Remove from exposure and move to fresh air immediately. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical aid.

Notes to Physician: Treat symptomatically and supportively.

Section 5 - Fire Fighting Measures

General Information: As in any fire, wear a self-contained breathing apparatus in pressure-demand, MSHA/NIOSH (approved or equivalent), and full protective gear. Substance is noncombustible.

Extinguishing Media: Substance is noncombustible; use agent most appropriate to extinguish surrounding fire.

Autoignition Temperature: Not applicable.

Flash Point: Not applicable.

Explosion Limits: Lower: None Reported

Explosion Limits: Upper: None Reported

NFPA Rating: health: 1; flammability: 0; instability: 0;

Section 6 - Accidental Release Measures

General Information: Use proper personal protective equipment as indicated in Section 8.

Spills/Leaks: Vacuum or sweep up material and place into a suitable disposal container. Clean up spills immediately, observing precautions in the Protective Equipment section. Avoid generating dusty conditions. Provide ventilation.

Section 7 - Handling and Storage

Handling: Wash thoroughly after handling. Remove contaminated clothing and wash before reuse. Use with adequate ventilation. Minimize dust generation and accumulation. Avoid contact with skin and eyes. Keep container tightly closed. Do not breathe dust.

Storage: Store in a cool, dry, well-ventilated area away from incompatible substances.

Section 8 - Exposure Controls, Personal Protection

Chemical Name	ACGIH	NIOSH	OSHA - Final PELs
Titanium dioxide	10 mg/m3	5000 mg/m3 IDLH	15 mg/m3 TWA (total dust)

OSHA Vacated PELs: Titanium dioxide: 10 mg/m3 TWA (total dust)

Engineering Controls:

Use adequate general or local exhaust ventilation to keep airborne concentrations below the permissible exposure limits.

Exposure Limits

Personal Protective Equipment

Eyes: Wear appropriate protective eyeglasses or chemical safety goggles as described by OSHA's eye and face protection regulations in 29 CFR 1910.133 or European Standard EN166.

Skin: Wear appropriate gloves to prevent skin exposure.

Clothing: Wear appropriate protective clothing to minimize contact with skin.

Respirators: Follow the OSHA respirator regulations found in 29 CFR 1910.134 or European Standard EN 149. Use a NIOSH/MSHA or European Standard EN 149 approved respirator if exposure limits are exceeded or if irritation or other symptoms are experienced.

Section 9 - Physical and Chemical Properties

Physical State: Powder
Color: white to off-white
Odor: odorless
pH: Not available
Vapor Pressure: Not available
Vapor Density: Not applicable.
Evaporation Rate: Not available
Viscosity: Not available
Boiling Point: 2900 deg C (5,252.00°F)
Freezing/Melting Point: 1855 deg C (3,371.00°F)
Decomposition Temperature: Not available
Solubility in water: Insoluble
Specific Gravity/Density: 3.84-4.26
Molecular Formula: $TiO2$
Molecular Weight: 79.88

Section 10 - Stability and Reactivity

Chemical Stability:	Stable under normal temperatures and pressures.
Conditions to Avoid:	Dust generation.
Incompatibilities with Other Materials	A violent or incandescent reaction with metals (aluminum, calcium, magnesium, potassium, sodium, zinc and lithium) may occur at high temperatures..
Hazardous Decomposition Products	None.
Hazardous Polymerization	Will not occur.

Section 11 - Toxicological Information

RTECS#:	CAS# 13463-67-7: XR2275000
LD50/LC50:	RTECS: Not available.
Carcinogenicity:	Titanium dioxide - IARC: Group 2B carcinogen
Other:	See actual entry in RTECS for complete information.

Section 12 - Ecological Information

Not available

Section 13 - Disposal Considerations

Dispose of in a manner consistent with federal, state, and local regulations.

Section 14 - Transport Information

US DOT
Shipping Name: Not regulated.
Hazard Class:
UN Number:
Packing Group:
Canada TDG
Shipping Name: Not regulated as a hazardous material
Hazard Class:
UN Number:
Packing Group:

Section 15 - Regulatory Information

European/International Regulations

European Labeling in Accordance with EC Directives

Hazard Symbols: XN

Risk Phrases:

R 40 Limited evidence of a carcinogenic effect.

Safety Phrases:

S 36/37 Wear suitable protective clothing and gloves.

WGK (Water Danger/Protection)

CAS# 13463-67-7: 0

Canada

CAS# 13463-67-7 is listed on Canada's DSL List

Canadian WHMIS Classifications: D2A

This product has been classified in accordance with the hazard criteria of the Controlled Products Regulations and the MSDS contains all of the information required by those regulations.

CAS# 13463-67-7 is not listed on Canada's Ingredient Disclosure List.

US Federal

TSCA

CAS# 13463-67-7 is listed on the TSCA Inventory.

Section 16 - Other Information

MSDS Creation Date: 12/12/1997

Revision #10 Date 7/20/2009

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

June 28, 2005

ACTION MEMORANDUM

SUBJECT: Inert Ingredient Tolerance Reassessment – Titanium Dioxide

FROM: Dan Rosenblatt, Chief
Minor Use, Inerts, and Emergency Response Branch

TO: Lois A. Rossi, Director
Registration Division

I. FQPA REASSESSMENT ACTION

Action: Reassessment of two (2) inert ingredient exemptions from the requirement of a tolerance.

Chemical and Use Summary: See table below.

Table 1. Tolerance Exemptions Being Reassessed in this Document

Tolerance Exemption Expression	40 CFR §	Use Pattern (Pesticidal)	CAS Reg No.	List Classification
Titanium dioxide (CAS Reg. No. 13463-67-7)	180.920[1/]	Pigment/coloring agent in plastic bags used to wrap growing banana (preharvest), colorant on seeds for planting	13463-67-7	4B
Titanium dioxide (CAS Reg. No. 13463-67-7)	180.930[2/]	Pigment/colorant in pesticide formulations for animal tag		

1. Residues listed in 40 CFR §180.920 [formerly 40 CFR§ 180.1001(d)] are exempted from the requirement of a tolerance when used as inert ingredients in pesticide formulations when applied to growing crops only.
2. Residues listed in 40 CFR §180.930 [formerly 40 CFR§ 180.1001(e)] are exempted from the requirement of a tolerance when used as inert ingredients in pesticide formulations when applied to animals.

Additionally, under 40 CFR §180.1195, titanium dioxide is exempted from the requirement of a tolerance for residues in or on growing crops, when used as an inert ingredient (UV protectant) in microencapsulated formulations of the insecticide lambda-cyhalothrin at no more than 3.0% by weight of the formulation. However this tolerance exemption was established after August 3, 1996, and is therefore not subject to the tolerance reassessment provision of FQPA.

List Classification Determination: Titanium dioxide is currently classified as a List 4B inert ingredient. Based on the non-bioavailability of titanium dioxide and lack of concern for adverse human health or nontarget organism effects, titanium dioxide can be reclassified as a List 4A inert ingredient.

II. MANAGEMENT CONCURRENCE

I concur with the reassessment of the two (2) exemptions from the requirement of a tolerance for the inert ingredient titanium dioxide, and with the List classification determination, as described above. I consider the exemption from the requirement of a tolerance for titanium dioxide established in 40 CFR §180.920 [formerly 40 CFR§180.1001(d)] and the exemption from the requirement of a tolerance for titanium dioxide established in 40 CFR §180.930 [formerly 40 CFR§180.1001(e)] to be maintained and reassessed as of the date of my signature, below. It should also be noted that while the exemption from the requirement of a tolerance for titanium dioxide established under 40 CFR 180.1195 is not part of this tolerance reassessment decision, the reasonable certainty of no harm safety finding made herein includes consideration of aggregate exposures to titanium dioxide resulting from use under all extant tolerance exemptions under 40 CFR Part 180. A Federal Register Notice regarding this tolerance exemption reassessment decision will be published in the near future.

Lois A. Rossi

Lois A. Rossi, Director
Registration Division

Date: July 11, 2005

cc: Debbie Edwards, SRRD
Joe Nevola, SRRD

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

June 28, 2005

MEMORANDUM

SUBJECT: Reassessment of the Exemptions from the Requirement of a Tolerance for Titanium Dioxide

FROM: Kerry Leifer, Inerts Team Leader
Minor Use, Inerts and Emergency Response Branch
Registration Division (7505C)

THRU: Pauline Wagner, Inerts Coordinator Pauline Wagner 6/28/05
Registration Division (7505C)

TO: Dan Rosenblatt, Chief
Minor Use, Inerts and Emergency Response Branch
Registration Division (7505C)

Background

Attached is the science assessment for titanium dioxide. The purpose of this document is to reassess two existing exemptions from the requirement of a tolerance for residues of this inert ingredient as required under the Food Quality Protection Act (FQPA). This assessment summarizes available information on the use, physical/chemical properties, toxicological effects, and exposure profiles of titanium dioxide. In performing this assessment, the Agency has relied extensively upon reviews of titanium dioxide previously performed by the European Commission Scientific Committee on Food (SCF), the Joint Expert Committee on Food Additives of the Food and Agriculture Organization/World Health Organization (JEFCA), and the European Food Safety Authority (EFSA).

Executive Summary

This report evaluates titanium dioxide (CAS Reg. No. 13463-67-7), a pesticide inert ingredient for which two exemptions from the requirement of a tolerance exists for its residues when used in pesticide formulations applied to growing crops only under 40 CFR §180.920 and in pesticide formulations applied to animals under 40 CFR §180.930. Titanium dioxide is a widely used inorganic white pigment that is produced from mined sources of titanium.

Titanium dioxide pigments are white inorganic pigments used primarily in the production of paints, printing inks, paper and plastic products. Titanium dioxide is also used in many white or colored products including foods, cosmetics, UV skin protection products, ceramics, fibers, and rubber products.

This hazard assessment relies upon peer-reviewed assessments of titanium dioxide performed by thye European Commission Scientific Committee on Food (SCF), the Joint Expert Committee on Food Additives of the Food and Agriculture Organization/World Health Organization (JECFA), and the European Food Safety Authority's (EFSA) Scientific Panel on Food Additives, Flavourings, Processing Aids and Materials in Contact with Food. Based on its evaluation of the available data on titanium dioxide, JECFA concluded that the establishment of an acceptable daily intake was unnecessary. In its safety review of certain food colorants, the SCF reaffirmed an earlier determination regarding the use of titanium dioxide as a colorant in foodstuffs and concluded that titanium dioxide was acceptable for general food use without the need for establishment of an acceptable daily intake. In its most recent evaluation of titanium dioxide, EFSA concurred with the JECFA assessment of titanium dioxide and concluded that the use of titanium dioxide would not pose any safety concerns. Both the JECFA and EFSA evaluations of titanium dioxide noted there is no absorption or tissue storage of titanium dioxide.

Titanium dioxide is not bioavailable as it is not absorbed via the gastrointestinal tract or through the skin. Inhalation exposure to high concentrations of titanium dioxide particles has been shown to result in pulmonary effects in rats, but these effects may be a rat-specific threshold phenomenon, possibly of little relevance to humans. Epidemiological data suggest that there is no carcinogenic effect associated with workplace exposure to titanium dioxide dust. Titanium dioxide is not carcinogenic in mice or rat dietary studies and no adverse effects were observed in chronic rat studies at concentrations up to 5% in the diet.

Based on the insoluble nature of titanium dioxide in water and the low acute toxicity of titanium dioxide to freshwater fish, there are no nontarget aquatic species risk concerns resulting from the use of titanium dioxide as an inert ingredient. Based on the lack of absorption, as well as no identified toxicological effects of concern in animal testing, there are no risk concerns for nontarget terrestrial organisms resulting from the use of titanium dioxide as an inert ingredient.

Taking into consideration all available information on titanium dioxide, it has been determined that there is a reasonable certainty that no harm to any population subgroup will result from aggregate exposure to titanium dioxide when considering dietary exposure and all other nonoccupational sources of pesticide exposure for which there is reliable information. Therefore, it is recommended that the exemptions from the requirement of a tolerance established for residues of titanium dioxide in/on raw agricultural commodities and animals can be considered reassessed as safe under section 408(q) of the FFDCA.

I. Introduction

This report evaluates titanium dioxide (CAS Reg. No. 13463-67-7), a pesticide inert ingredient for which two exemptions from the requirement of a tolerance exist for its residues when used in pesticide formulations applied to growing crops only under 40 CFR §180.920 and in pesticide formulations applied to animals under 40 CFR §180.930. An exemption from the requirement of a tolerance was established for titanium dioxide under 40 CFR §180.1195 for use as an inert ingredient (UV protectant) in microencapsulated formulations of lambda-cyhalothrin on March 25, 1998 (EPA 1998), however that rule did not specifically address the reassessment of the two above-noted tolerance exemptions for titanium dioxide.

Titanium dioxide is a widely used inorganic white pigment that is produced from mined sources of titanium, with 98% of all mined titanium used in the production of titanium dioxide. The most commercially significant mineral forms of titanium dioxide are rutile and anatase (Terran 1997). The production of titanium dioxide pigment in the United States in 2003 was 1.4 million metric tons (Gambogi 2003).

II. Use Information

Pesticides

The two tolerance exemptions for titanium dioxide being reassessed in this document are given in Table 1 below.

Table 1. Tolerance Exemptions Being Reassessed in this Document

Tolerance Exemption Expression	40 CFR §	Use Pattern (Pesticidal)	CAS Reg No.	List Classification
Titanium dioxide (CAS Reg No. 13463-67-7)	180.920[1/]	Pigment/coloring agent in plastic bags used to wrap growing banana (preharvest), colorant on seeds for planting	13463-67-7	4B
Titanium dioxide (CAS Reg. No. 13463-67-7)	180.930[2/]	Pigment/colorant in pesticide formulations for animal tag		

1. Residues listed in 40 CFR §180.920 [formerly 40 CFR§ 180.1001(d)] are exempted from the requirement of a tolerance when used as inert ingredients in pesticide formulations when applied to growing crops only.

2. Residues listed in 40 CFR §180.930 [formerly 40 CFR§ 180.1001(e)] are exempted from the requirement of a tolerance when used as inert ingredients in pesticide formulations when applied to animals.

Additionally, under 40 CFR §180.1195, titanium dioxide is exempted from the requirement of a tolerance for residues in or on growing crops, when used as an inert ingredient (UV protectant) in microencapsulated formulations of the insecticide lambda-cyhalothrin at no more than 3.0% by weight of the formulation (EPA 1998). Since this tolerance exemption was established after August 3, 1996, it is not subject to the tolerance reassessment provision of FQPA.

Other Uses

Titanium dioxide pigments are white inorganic pigments used primarily in the production of paints, printing inks, paper and plastic products. Titanium dioxide is also used in many white or colored products including foods, cosmetics, UV skin protection products, ceramics, fibers, and rubber products. Titanium dioxide provides opacity and imparts whiteness and brightness to the products in which it is used, as well as affording protection from UV degradation (CEFIC 2002).

Titanium dioxide is approved by the Food and Drug Administration (FDA) as a color additive exempt from certification for the following uses: under 21 CFR §73.575 for coloring foods at levels up to one percent by weight; under 21 CFR §73.1575 for coloring ingested and externally applied drugs generally; and under 21 CFR §73.2575 for use in cosmetics, including cosmetics intended for use in the area of the eye.

III. Physical and Chemical Properties

Some of the physical and chemical characteristics of titanium dioxide are given in Table 2. below.

Table 2. Titanium Dioxide Physical and Chemical Properties

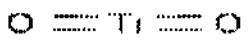
Parameter	Value	Source
Structure		ChemIDplus 2005
Physical Form	Solid	HSDB 2005

Table 2. Titanium Dioxide Physical and Chemical Properties		
Parameter	**Value**	**Source**
Molecular Weight	79.865	ChemIDplus 2005
Water Solubility	none	IPCS 1993
Melting Point	1843 ° C (M)	HSDB 2005
Vapor Pressure	Not applicable	
Henry's Law Constant	Not applicable	
Octanol-Water Partition Coefficient (K_{OW})	Not applicable	

IV. Hazard Assessment

A. Hazard Profile

This hazard assessment primarily relies upon peer-reviewed assessments of titanium dioxide performed by European Commission Scientific Committee on Food (SCF), the Joint Expert Committee on Food Additives of the Food and Agriculture Organization/World Health Organization (JECFA), and the European Food Safety Authority's (EFSA) Scientific Panel on Food Additives, Flavourings, Processing Aids and Materials in Contact with Food.

The JECFA evaluation of titanium dioxide states that "Titanium dioxide is a very insoluble compound. The studies in several species, including man, show neither significant absorption nor tissue storage following ingestion of titanium dioxide." Based on its evaluation of the available data on titanium dioxide, JECFA concluded that the "Establishment of an acceptable daily intake[1] for man is considered unnecessary" (JECFA 1969).

In its safety review of certain food colorants, the SCF reaffirmed an earlier determination regarding the use of titanium dioxide as a colorant in foodstuffs and concluded that titanium dioxide was acceptable for general food use with no established ADI (SCF 1977). The responsibilities for European Commission risk assessments for food additives is now the responsibility of the EFSA which, in its most recent evaluation of titanium dioxide, concurred with the JECFA assessment of titanium dioxide and concluded that the use of titanium dioxide would not pose any safety concerns (EFSA 2004).

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[1] ADI (Acceptable Daily Intake): An estimate by JECFA of the amount of a food additive, expressed on a body weight basis, that can be ingested daily over a lifetime without appreciable health risk

Titanium dioxide is not dermally absorbed by humans (Plfucker et al 2001). Titanium dioxide is a frequently used compound in lung clearance studies, where a biologically inert substance is required, however inhalation of high concentrations of fine or ultrafine titanium dioxide particles has been shown to result in pulmonary inflammation, fibrosis, and lung tumors in rats (Lee et al 1985). In contrast to the results in rats, inhalation effects were not observed in mice and hamsters and may be a rat-specific threshold phenomenon, dependent upon lung overloading at high exposure concentrations and possibly of little relevance to humans. Epidemiological data suggest that there is no carcinogenic effect associated with workplace exposure to titanium dioxide dust (Hext et al 2005).

B. Toxicological Data

The EFSA evaluation of titanium dioxide noted the toxicological database considered by JECFA and referenced additional key toxicological data on chronic toxicity and carcinogenicity. The EFSA evaluation of the additional toxicological data reported "a NCI carcinogenicity study was conducted in groups of 50 per sex of Fischer 344 rats and B6C3F1 mice dosed at 0, 25000 and 50000 mg titanium dioxide /kg diet for 103 weeks (NCI, 1979). Increased incidences of thyroid C-cell adenomas or carcinomas were observed in female rats but these increases were neither statistically significant nor considered to be related to administration of the test compound. Tumour incidences in the other groups were not significantly higher than in controls. A chronic dietary study administration of titanium dioxide coated mica at 0, 1, 2 and 5% in Fischer 344 rats for 130 weeks showed no toxicological or carcinogenic effects (Bernard et al., 1990)."

C. Metabolism And Pharmacokinetics

Both the JECFA and EFSA evaluations of titanium dioxide noted that there is no absorption or tissue storage of titanium dioxide. The World Health Organization (WHO) Environmental Health Criteria for titanium, an evaluation of the effects of titanium on human health and the quality of the environment, states that "titanium compounds are poorly absorbed from the gastrointestinal tract, which is the main route of exposure for the general population" (WHO 1982).

There is no dermal absorption of titanium dioxide. Inhalation effects resulting from titanium dioxide are limited to localized lung effects Adverse effects resulting from inhalation studies of titanium dioxide have been confined to the respiratory tract and lung-associated lymphatic tissues (NAS 1999).

D. Special Considerations for Infants and Children

Based on the lack of absorption, history of safe use as a pigment and food additive, low toxicity, and lack of concern for human health effects, a safety factor analysis has not been used to assess the risks resulting from the use of titanium dioxide as a pesticide inert ingredient and an additional tenfold safety factor for the protection of infants and children is unnecessary.

V. Exposure Assessment

Titanium dioxide is not absorbed via the oral or dermal routes of exposure, therefore no further oral or dermal exposure assessment is necessary. Exposures to high concentrations of fine or ultrafine titanium dioxide particles have been shown to result in pulmonary effects in rats but is likely a rat-specific threshold phenomenon, dependent upon lung overloading at high exposure concentrations and possibly of little relevance to humans. Since the pesticide inert ingredient use of titanium dioxide is as a pigment in which the titanium dioxide is bound in a polymeric matrix and not present as particulate titanium dioxide, there would be no inhalation exposure to titanium dioxide particles resulting from its use as a pesticide inert ingredient and no further inhalation exposure assessment is necessary.

VI. Aggregate Exposures

In examining aggregate exposure, FFDCA section 408 directs EPA to consider available information concerning exposures from the pesticide residue in food and all other non-occupational exposures, including drinking water from ground water or surface water and exposure through pesticide use in gardens, lawns, or buildings (residential and other indoor uses).

For titanium dioxide, a qualitative assessment for all pathways of human exposure (food, drinking water, and residential) is appropriate given the general lack of bioavailability of titanium dioxide, its insolubility in water, and the lack of human health concerns associated with exposure to titanium dioxide.

VII. Cumulative Exposure

Section 408(b)(2)(D)(v) of the FFDCA requires that, when considering whether to establish, modify, or revoke a tolerance, the Agency consider "available information" concerning the cumulative effects of a particular pesticide's residues and "other substances that have a common mechanism of toxicity."

Unlike other pesticides for which EPA has followed a cumulative risk approach based on a common mechanism of toxicity, EPA has not made a common mechanism of toxicity finding as to titanium dioxide and any other substances and this material does not appear to produce a toxic metabolite produced by other substances. For the purposes of this tolerance action, therefore, EPA has not assumed that titanium dioxide has a common mechanism of toxicity with other substances. For information regarding EPA's efforts to determine which chemicals have a common mechanism of toxicity and to evaluate the cumulative effects of such chemicals, see the policy statements released by EPA concerning common mechanism determinations and procedures for cumulating effects from substances found to have a common mechanism on EPA's website at http://www.epa.gov/pesticides/cumulative/

VIII. Environmental Fate Characterization/Drinking Water Considerations

Titanium dioxide is a stable compound that is insoluble in water and therefore would not be expected to be present in drinking water sources as a result of pesticide inert ingredient use.

IX. Human Health Risk Characterization

Evaluations of titanium dioxide by JECFA, SCF, and EFSA have each concluded that there are no safety concerns associated with the use of titanium dioxide as a food additive at levels ranging up to 3%. Taking into consideration all available information on titanium dioxide, it has been determined that there is a reasonable certainty that no harm to any population subgroup will result from aggregate exposure to titanium dioxide when considering dietary exposure and all other nonoccupational sources of pesticide exposure for which there is reliable information. Therefore, it is recommended that the exemptions from the requirement of a tolerance established for residues of titanium dioxide in/on raw agricultural commodities and animals can be considered reassessed as safe under section 408(q) of the FFDCA.

X. Ecotoxicity and Ecological Risk Characterization

The available ecotoxicity data on titanium dioxide are primarily limited to acute aquatic toxicity studies. The acute aquatic LC_{50} of titanium dioxide in fathead minnows is >1000 mg/L (ECOTOX 2002). Based on the insoluble nature of titanium dioxide in water and the low acute toxicity of titanium dioxide to freshwater fish, there are no nontarget aquatic species risk concerns resulting from the use of titanium dioxide as an inert ingredient. Based on the lack of absorption as well as no identified toxicological effects of concern in animal testing, there are also no risk concerns for nontarget terrestrial organisms resulting from the use of titanium dioxide as an inert ingredient.

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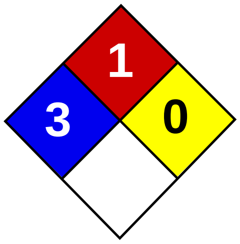

Health	**3**
Fire	**1**
Reactivity	**0**
Personal Protection	

Material Safety Data Sheet

Lactic Acid, 85% MSDS

Section 1: Chemical Product and Company Identification

Product Name: Lactic Acid, 85%

Catalog Codes: SLL1333, SLL1120

CAS#: 50-21-5

RTECS: OD2800000

TSCA: TSCA 8(b) inventory: Lactic Acid

CI#: Not available.

Synonym: 2-Hydroxypropanoic Acid; 2-Hydroxypropionic acid; Racemic lactic acid; Ordinary lactic acid; Propanoic acid, 2-hydroxy-; Lactic Acid is a mixture of Lactic Acid (C3H6O3) and Lactic Acid Lactate (C6H10O5)

Chemical Name: Lactic Acid

Chemical Formula: C3-H6-O3

Contact Information:

Sciencelab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396

US Sales: **1-800-901-7247**
International Sales: **1-281-441-4400**

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:
1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Lactic Acid	50-21-5	81 - 90

Toxicological Data on Ingredients: Lactic Acid,: ORAL (LD50): Acute: 3543 mg/kg [Rat]. 4875 mg/kg [Mouse]. DERMAL (LD50): Acute: 2000 mg/kg [Rabbit].

Section 3: Hazards Identification

Potential Acute Health Effects:
Very hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Slightly hazardous in case of skin contact (corrosive), of eye contact (corrosive). Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

Potential Chronic Health Effects:
CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Mutagenic for bacteria and/or yeast. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. Repeated or prolonged contact with spray mist

may produce chronic eye irritation and severe skin irritation. Repeated or prolonged exposure to spray mist may produce respiratory tract irritation leading to frequent attacks of bronchial infection.

Section 4: First Aid Measures

Eye Contact:
Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention immediately.

Skin Contact:
In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Cover the irritated skin with an emollient. Cold water may be used.Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention immediately.

Serious Skin Contact:
Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek immediate medical attention.

Inhalation:
If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention immediately.

Serious Inhalation:
Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. WARNING: It may be hazardous to the person providing aid to give mouth-to-mouth resuscitation when the inhaled material is toxic, infectious or corrosive. Seek immediate medical attention.

Ingestion:
Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention if symptoms appear.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: May be combustible at high temperature.

Auto-Ignition Temperature: Not available.

Flash Points: CLOSED CUP: 112.78°C (235°F).

Flammable Limits: Not available.

Products of Combustion: These products are carbon oxides (CO, CO2).

Fire Hazards in Presence of Various Substances:
Slightly flammable to flammable in presence of open flames and sparks, of heat. Non-flammable in presence of shocks.

Explosion Hazards in Presence of Various Substances:
Risks of explosion of the product in presence of mechanical impact: Not available. Risks of explosion of the product in presence of static discharge: Not available.

Fire Fighting Media and Instructions:
SMALL FIRE: Use DRY chemical powder. LARGE FIRE: Use water spray, fog or foam. Do not use water jet.

Special Remarks on Fire Hazards: Not available.

Special Remarks on Explosion Hazards: Not available.

Section 6: Accidental Release Measures

Small Spill:
Dilute with water and mop up, or absorb with an inert dry material and place in an appropriate waste disposal container. If necessary: Neutralize the residue with a dilute solution of sodium carbonate.

Large Spill:
Corrosive liquid. Stop leak if without risk. If the product is in its solid form: Use a shovel to put the material into a convenient waste disposal container. If the product is in its liquid form: Absorb with DRY earth, sand or other non-combustible material. Do not get water inside container. Absorb with an inert material and put the spilled material in an appropriate waste disposal. Do not touch spilled material. Use water spray curtain to divert vapor drift. Prevent entry into sewers, basements or confined areas; dike if needed. Eliminate all ignition sources. Call for assistance on disposal. Neutralize the residue with a dilute solution of sodium carbonate.

Section 7: Handling and Storage

Precautions:
Keep locked up.. Keep container dry. Keep away from heat. Keep away from sources of ignition. Empty containers pose a fire risk, evaporate the residue under a fume hood. Ground all equipment containing material. Do not ingest. Do not breathe gas/ fumes/ vapor/spray. Never add water to this product. In case of insufficient ventilation, wear suitable respiratory equipment. If ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes. Keep away from incompatibles such as oxidizing agents.

Storage: Keep container tightly closed. Keep container in a cool, well-ventilated area.

Section 8: Exposure Controls/Personal Protection

Engineering Controls:
Provide exhaust ventilation or other engineering controls to keep the airborne concentrations of vapors below their respective threshold limit value. Ensure that eyewash stations and safety showers are proximal to the work-station location.

Personal Protection:
Face shield. Full suit. Vapor respirator. Be sure to use an approved/certified respirator or equivalent. Gloves. Boots.

Personal Protection in Case of a Large Spill:
Splash goggles. Full suit. Vapor respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits: Not available.

Section 9: Physical and Chemical Properties

Physical state and appearance: Liquid. (Viscous/Syrupy liquid.)

Odor: Acrid (Slight.)

Taste: Acrid.

Molecular Weight: 90.08 g/mole

Color: Colorless to light yellow.

pH (1% soln/water): 2 [Acidic.]

Boiling Point: 122°C (251.6°F)

Melting Point: 16.8°C (62.2°F)

Critical Temperature: Not available.

Specific Gravity: 1.249 (Water = 1)

Vapor Pressure: 0 kPa (@ 20°C)

Vapor Density: >1 (Air = 1)

Volatility: Not available.

Odor Threshold: Not available.

Water/Oil Dist. Coeff.: The product is more soluble in water; log(oil/water) = -0.7

Ionicity (in Water): Not available.

Dispersion Properties: See solubility in water, diethyl ether.

Solubility:
Soluble in cold water, hot water. Partially soluble in diethyl ether. Soluble in Furfurol, alcohol. Practically insoluble in chloroform, petroleum ether, carbon disulfide.

Section 10: Stability and Reactivity Data

Stability: The product is stable.

Instability Temperature: Not available.

Conditions of Instability: Excess heat, incompatible materials

Incompatibility with various substances: Reactive with oxidizing agents, alkalis.

Corrosivity:
Slightly corrosive in presence of aluminum, of copper, of stainless steel(304), of stainless steel(316). Non-corrosive in presence of glass.

Special Remarks on Reactivity: Not available.

Special Remarks on Corrosivity:
Caustic in concentrated solutions. Severe corrosive effect on brass. Minor corrosive effect on bronze.

Polymerization: Will not occur.

Section 11: Toxicological Information

Routes of Entry: Absorbed through skin. Eye contact.

Toxicity to Animals:
Acute oral toxicity (LD50): 3543 mg/kg [Rat]. Acute dermal toxicity (LD50): 2000 mg/kg [Rabbit].

Chronic Effects on Humans: MUTAGENIC EFFECTS: Mutagenic for bacteria and/or yeast.

Other Toxic Effects on Humans:
Extremely hazardous in case of inhalation (lung corrosive). Very hazardous in case of skin contact (irritant), of ingestion, . Slightly hazardous in case of skin contact (corrosive), of eye contact (corrosive).

Special Remarks on Toxicity to Animals: Not available.

Special Remarks on Chronic Effects on Humans:
May affect genetic material. May cause adverse reproductive effects and birth defects based on animal data.

Special Remarks on other Toxic Effects on Humans:
Acute Potential Health Effects: Skin: Causes severe skin irritation. Possible burns or ulcerations upon prolonged overexposure. May cause skin rash (in milder cases). It may be absorbed by the skin Eyes: Causes severe irritation and possible burns. May cause chemical conjunctivitis and corneal damage. Inhalation: Causes severe respiratory tract and mucous membrane irritation with possible burns. Inhalation may be fatal as a result of spasm, inflammation, edema of the larynx and bronchi, chemical pneumonitis and pulmonary edema. Aspiration may lead to pulmonary edema. Other symptoms may include shortness of breath, coughing, and sore throat. Ingestion: May cause gastrointestinal tract irritation with nausea,

vomiting, diarrhea, and possible burns (in the throat, mouth, and stomach). May cause severe and permanent damage to the digestive tract. May cause perforation of the digestive tract. May also cause shortness of breath and in severe cases may produce cyanosis and vascular collapse. Chronic Potential Health Effects: Skin: Prolonged or repeated skin contact/absorption may affect the brain, urinary system and blood.

Section 12: Ecological Information

Ecotoxicity: Not available.

BOD5 and COD: Not available.

Products of Biodegradation:
Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

Toxicity of the Products of Biodegradation: The products of degradation are less toxic than the product itself.

Special Remarks on the Products of Biodegradation: Not available.

Section 13: Disposal Considerations

Waste Disposal:
Waste must be disposed of in accordance with federal, state and local environmental control regulations.

Section 14: Transport Information

DOT Classification: Class 8: Corrosive material

Identification: : Corrosive liquid, acidic, organic, n.o.s. (Lactic acid) UNNA: 3265 PG: III

Special Provisions for Transport: Not available.

Section 15: Other Regulatory Information

Federal and State Regulations: TSCA 8(b) inventory: Lactic Acid

Other Regulations:
OSHA: Hazardous by definition of Hazard Communication Standard (29 CFR 1910.1200). EINECS: This product is on the European Inventory of Existing Commercial Chemical Substances.

Other Classifications:

WHMIS (Canada): CLASS E: Corrosive liquid.

DSCL (EEC):
R34- Causes burns. S1/2- Keep locked up and out of the reach of children. S24/25- Avoid contact with skin and eyes. S26- In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. S27- Take off immediately all contaminated clothing. S36/37/39- Wear suitable protective clothing, gloves and eye/face protection. S45- In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible). S46- If swallowed, seek medical advice immediately and show this container or label.

HMIS (U.S.A.):

Health Hazard: 3

Fire Hazard: 1

Reactivity: 0

Personal Protection:

National Fire Protection Association (U.S.A.):

Health: 3

Flammability: 1

Reactivity: 0

Specific hazard:

Protective Equipment:
Gloves. Full suit. Vapor respirator. Be sure to use an approved/certified respirator or equivalent. Wear appropriate respirator when ventilation is inadequate. Face shield.

Section 16: Other Information

References: Not available.

Other Special Considerations: Not available.

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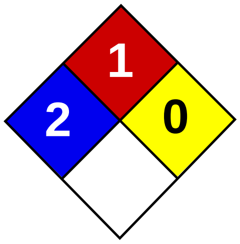
Last Updated: 11/01/2010 12:00 PM



Health	2
Fire	1
Reactivity	0
Personal Protection	E

Material Safety Data Sheet

Adipic acid MSDS

Section 1: Chemical Product and Company Identification

Product Name: Adipic acid

Catalog Codes: SLA3658

CAS#: 124-04-9

RTECS: AU8400000

TSCA: TSCA 8(b) inventory: Adipic acid

CI#: Not available.

Synonym: Hexanedioic acid; 1,4-Butane Dicarboxylic Acid

Chemical Name: Adipic Acid

Chemical Formula: HOOC(CH2)4COOH

Contact Information:

Sciencelab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396

US Sales: **1-800-901-7247**
International Sales: **1-281-441-4400**

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:
1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Adipic acid	124-04-9	100

Toxicological Data on Ingredients: Adipic acid: ORAL (LD50): Acute: >11000 mg/kg [Rat]. 1900 mg/kg [Mouse]. >11000 mg/kg [Rabbit].

Section 3: Hazards Identification

Potential Acute Health Effects: Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation.

Potential Chronic Health Effects:
Slightly hazardous in case of inhalation (lung sensitizer). CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. The substance may be toxic to the nervous system, gastrointestinal tract. Repeated or prolonged exposure to the substance can produce target organs damage.

Section 4: First Aid Measures

Eye Contact:

Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention.

Skin Contact:
In case of contact, immediately flush skin with plenty of water. Cover the irritated skin with an emollient. Remove contaminated clothing and shoes. Cold water may be used.Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention.

Serious Skin Contact:
Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek medical attention.

Inhalation:
If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

Serious Inhalation: Not available.

Ingestion:
Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention if symptoms appear.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: May be combustible at high temperature.

Auto-Ignition Temperature: 420°C (788°F)

Flash Points: CLOSED CUP: 196°C (384.8°F).

Flammable Limits: Not available.

Products of Combustion: These products are carbon oxides (CO, CO2).

Fire Hazards in Presence of Various Substances:
Slightly flammable to flammable in presence of heat. Non-flammable in presence of shocks.

Explosion Hazards in Presence of Various Substances:
Risks of explosion of the product in presence of mechanical impact: Not available. Slightly explosive in presence of open flames and sparks, of heat.

Fire Fighting Media and Instructions:
SMALL FIRE: Use DRY chemical powder. LARGE FIRE: Use water spray, fog or foam. Do not use water jet.

Special Remarks on Fire Hazards: Not available.

Special Remarks on Explosion Hazards: Dust generation can form an explosive mixture if dispersed in a sufficient quantity of air.

Section 6: Accidental Release Measures

Small Spill:
Use appropriate tools to put the spilled solid in a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and dispose of according to local and regional authority requirements.

Large Spill:
Use a shovel to put the material into a convenient waste disposal container. Be careful that the product is not present at a concentration level above TLV. Check TLV on the MSDS and with local authorities.

Section 7: Handling and Storage

Precations:

Keep away from heat. Keep away from sources of ignition. Empty containers pose a fire risk, evaporate the residue under a fume hood. Ground all equipment containing material. Do not ingest. Do not breathe dust. Wear suitable protective clothing. In case of insufficient ventilation, wear suitable respiratory equipment. If ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes. Keep away from incompatibles such as oxidizing agents.

Storage: Keep container tightly closed. Keep container in a cool, well-ventilated area. Do not store above 25°C (77°F).

Section 8: Exposure Controls/Personal Protection

Engineering Controls:

Use process enclosures, local exhaust ventilation, or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fume or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.

Personal Protection:

Splash goggles. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.

Personal Protection in Case of a Large Spill:

Splash goggles. Full suit. Dust respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits:

TWA: 5 (mg/m3) from ACGIH (TLV) [United States] Inhalation Consult local authorities for acceptable exposure limits.

Section 9: Physical and Chemical Properties

Physical state and appearance: Solid. (crystalline powder.)

Odor: Odorless.

Taste: Tart

Molecular Weight: 146.14 g/mole

Color: White.

pH (1% soln/water): Not available.

Boiling Point: 337.5°C (639.5°F)

Melting Point: 152°C (305.6°F)

Critical Temperature: Not available.

Specific Gravity: 1.36 (Water = 1)

Vapor Pressure: Not applicable.

Vapor Density: 5.04 (Air = 1)

Volatility: Not available.

Odor Threshold: Not available.

Water/Oil Dist. Coeff.: The product is equally soluble in oil and water; log(oil/water) = 0.1

Ionicity (in Water): Not available.

Dispersion Properties: See solubility in water, methanol, acetone.

Solubility:

Easily soluble in methanol. Soluble in hot water, acetone. Partially soluble in cold water. Insoluble in Acetic acid, Petroleum Benzin, Benzene, Petroleum Ether. Slightly soluble in Cyclohexane. Freely soluble in Ethanol.

Section 10: Stability and Reactivity Data

Stability: The product is stable.

Instability Temperature: Not available.

Conditions of Instability: Excess heat, excess dust generation, ignition sources, incompatible materials

Incompatibility with various substances: Reactive with oxidizing agents.

Corrosivity: Not available.

Special Remarks on Reactivity: Not available.

Special Remarks on Corrosivity: Aqueous solutions of Adipic acid are corrosive

Polymerization: Will not occur.

Section 11: Toxicological Information

Routes of Entry: Inhalation. Ingestion.

Toxicity to Animals: Acute oral toxicity (LD50): 1900 mg/kg [Mouse].

Chronic Effects on Humans: May cause damage to the following organs: the nervous system, gastrointestinal tract.

Other Toxic Effects on Humans: Hazardous in case of skin contact (irritant), of ingestion, of inhalation.

Special Remarks on Toxicity to Animals: Not available.

Special Remarks on Chronic Effects on Humans: Not available.

Special Remarks on other Toxic Effects on Humans:
Acute Potential Health Effects: May cause skin irritation. Eyes: May cause eye irritation. Inhalation: Expected to be a low hazard for ususal industrial handling. May cause respiratory tract. Symptoms may include coughing, sneezing, and blood-tinged mucous. Ingestion: Expected to be a low ingestion hazard if small amounts (less than a mouthful) are ingested. Ingestion of large amounts may cause gastrointestinal tract irritation with hypermotility, and diarrhea. May also affect behavior (somnolence, convulsions), and metabolism, and may cause hemorrhaging. Chronic Potential Health Effects: Inhalation: Repeated or prolonged contact by inhalation may cause asthma.

Section 12: Ecological Information

Ecotoxicity: Not available.

BOD5 and COD: Not available.

Products of Biodegradation:
Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

Toxicity of the Products of Biodegradation: The product itself and its products of degradation are not toxic.

Special Remarks on the Products of Biodegradation: Not available.

Section 13: Disposal Considerations

Waste Disposal:
Waste must be disposed of in accordance with federal, state and local environmental control regulations.

Section 14: Transport Information

DOT Classification: Not a DOT controlled material (United States).

Identification: : Adipic Acid UNNA: NA9077 PG: III

Special Provisions for Transport: Not applicable.

Section 15: Other Regulatory Information

Federal and State Regulations:
Connecticut hazardous material survey.: Adipic acid Illinois chemical safety act: Adipic acid New York release reporting list: Adipic acid Rhode Island RTK hazardous substances: Adipic acid Pennsylvania RTK: Adipic acid Massachusetts RTK: Adipic acid Massachusetts spill list: Adipic acid New Jersey: Adipic acid New Jersey spill list: Adipic acid Louisiana spill reporting: Adipic acid TSCA 8(b) inventory: Adipic acid CERCLA: Hazardous substances.: Adipic acid: 5000 lbs. (2268 kg)

Other Regulations:
OSHA: Hazardous by definition of Hazard Communication Standard (29 CFR 1910.1200). EINECS: This product is on the European Inventory of Existing Commercial Chemical Substances.

Other Classifications:

WHMIS (Canada): Not controlled under WHMIS (Canada).

DSCL (EEC):
R36/38- Irritating to eyes and skin. S2- Keep out of the reach of children. S46- If swallowed, seek medical advice immediately and show this container or label.

HMIS (U.S.A.):

Health Hazard: 2

Fire Hazard: 1

Reactivity: 0

Personal Protection: E

National Fire Protection Association (U.S.A.):

Health: 2

Flammability: 1

Reactivity: 0

Specific hazard:

Protective Equipment:
Gloves. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Splash goggles.

Section 16: Other Information

References: Not available.

Other Special Considerations: Not available.

Created: 10/11/2005 11:13 AM

Last Updated: 11/01/2010 12:00 PM

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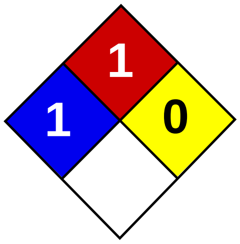


Health	1
Fire	1
Reactivity	0
Personal Protection	E

Material Safety Data Sheet
Azelaic Acid MSDS

Section 1: Chemical Product and Company Identification

Product Name: Azelaic Acid

Catalog Codes: SLA3673

CAS#: 123-99-9

RTECS: CM1980000

TSCA: TSCA 8(b) inventory: Azelaic Acid

CI#: Not available.

Synonym: Nonanedioic Acid; 1,7-Heptanedicarboxylic Acid

Chemical Name: Azelaic Acid

Chemical Formula: C9-H16-O4

Contact Information:

Sciencelab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396

US Sales: **1-800-901-7247**
International Sales: **1-281-441-4400**

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:
1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Azelaic Acid	123-99-9	100

Toxicological Data on Ingredients: Not applicable.

Section 3: Hazards Identification

Potential Acute Health Effects: Slightly hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation.

Potential Chronic Health Effects:
CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Classified Development toxin [None.]. Repeated or prolonged exposure is not known to aggravate medical condition.

Section 4: First Aid Measures

Eye Contact:
Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention if irritation occurs.

Skin Contact:
Wash with soap and water. Cover the irritated skin with an emollient. Get medical attention if irritation develops. Cold water may be used.

Serious Skin Contact: Not available.

Inhalation:
If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

Serious Inhalation: Not available.

Ingestion:
Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention if symptoms appear.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: May be combustible at high temperature.

Auto-Ignition Temperature: Not available.

Flash Points: CLOSED CUP: 210°C (410°F).

Flammable Limits: Not available.

Products of Combustion: These products are carbon oxides (CO, CO2).

Fire Hazards in Presence of Various Substances: Slightly flammable to flammable in presence of heat.

Explosion Hazards in Presence of Various Substances:
Risks of explosion of the product in presence of mechanical impact: Not available. Risks of explosion of the product in presence of static discharge: Not available.

Fire Fighting Media and Instructions:
SMALL FIRE: Use DRY chemical powder. LARGE FIRE: Use water spray, fog or foam. Do not use water jet.

Special Remarks on Fire Hazards: Not available.

Special Remarks on Explosion Hazards: Not available.

Section 6: Accidental Release Measures

Small Spill:
Use appropriate tools to put the spilled solid in a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and dispose of according to local and regional authority requirements.

Large Spill:
Use a shovel to put the material into a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and allow to evacuate through the sanitary system.

Section 7: Handling and Storage

Precautions:
Keep away from heat. Keep away from sources of ignition. Ground all equipment containing material. Do not ingest. Do not breathe dust. If ingested, seek medical advice immediately and show the container or the label. Keep away from incompatibles such as oxidizing agents.

Storage:

Keep container tightly closed. Keep container in a cool, well-ventilated area. Sensitive to light. Store in light-resistant containers.

Section 8: Exposure Controls/Personal Protection

Engineering Controls:
Use process enclosures, local exhaust ventilation, or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fume or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.

Personal Protection: Safety glasses. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.

Personal Protection in Case of a Large Spill:
Splash goggles. Full suit. Dust respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits: Not available.

Section 9: Physical and Chemical Properties

Physical state and appearance: Solid. (Flakes solid.)

Odor: Not available.

Taste: Not available.

Molecular Weight: 188.22 g/mole

Color: White.

pH (1% soln/water): Not available.

Boiling Point: 286.5°C(547.7°F) @ 100 mm Hg; 265 C @ 50 mm Hg; 237 C @ 15 mm Hg; 225 C @ 10 mm Hg

Melting Point: 106.5°C (223.7°F)

Critical Temperature: Not available.

Specific Gravity: Not available.

Vapor Pressure: Not applicable.

Vapor Density: Not available.

Volatility: Not available.

Odor Threshold: Not available.

Water/Oil Dist. Coeff.: Not available.

Ionicity (in Water): Not available.

Dispersion Properties: See solubility in water.

Solubility:
Partially soluble in cold water. Solubility in water: 1 g/l @ 1 C; 2.4 g/l @ 20 C.; 8.2 g/l @ 50 C; 22 g/l @ 65 C.

Section 10: Stability and Reactivity Data

Stability: The product is stable.

Instability Temperature: Not available.

Conditions of Instability: Excess heat, incompatible materials, light

Incompatibility with various substances: Reactive with oxidizing agents.

Corrosivity: Non-corrosive in presence of glass.

Special Remarks on Reactivity: Not available.

Special Remarks on Corrosivity: Not available.

Polymerization: Will not occur.

Section 11: Toxicological Information

Routes of Entry: Dermal contact. Inhalation. Ingestion.

Toxicity to Animals: Acute oral toxicity (LD50): >5000 mg/kg [Rat].

Chronic Effects on Humans: DEVELOPMENTAL TOXICITY: Classified Development toxin [None.].

Other Toxic Effects on Humans: Slightly hazardous in case of skin contact (irritant), of ingestion, of inhalation.

Special Remarks on Toxicity to Animals: Not available.

Special Remarks on Chronic Effects on Humans: Not available.

Special Remarks on other Toxic Effects on Humans:
Acute Potential Health Effects: Skin: May cause mild skin irritation. Eyes: May cause mild eye irritation. Inhalation: May cause respiratory tract irritation. Ingestion: May cause digestive tract irritation.

Section 12: Ecological Information

Ecotoxicity: Not available.

BOD5 and COD: Not available.

Products of Biodegradation:
Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

Toxicity of the Products of Biodegradation: The product itself and its products of degradation are not toxic.

Special Remarks on the Products of Biodegradation: Not available.

Section 13: Disposal Considerations

Waste Disposal:
Waste must be disposed of in accordance with federal, state and local environmental control regulations.

Section 14: Transport Information

DOT Classification: Not a DOT controlled material (United States).

Identification: Not applicable.

Special Provisions for Transport: Not applicable.

Section 15: Other Regulatory Information

Federal and State Regulations: TSCA 8(b) inventory: Azelaic Acid

Other Regulations: EINECS: This product is on the European Inventory of Existing Commercial Chemical Substances.

Other Classifications:

WHMIS (Canada): Not controlled under WHMIS (Canada).

DSCL (EEC):
This product is not classified according to the EU regulations. S24/25- Avoid contact with skin and eyes.

HMIS (U.S.A.):

Health Hazard: 1

Fire Hazard: 1

Reactivity: 0

Personal Protection: E

National Fire Protection Association (U.S.A.):

Health: 1

Flammability: 1

Reactivity: 0

Specific hazard:

Protective Equipment:
Gloves. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Safety glasses.

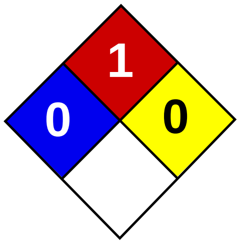
Section 16: Other Information

References:
-Manufacturer's Material Safety Data Sheet. -Merck Index, 13th ed. -Registery of Toxic Effects of Chemical Substances (RTECS) -Ariel GlobalView

Other Special Considerations: Not available.

Created: 10/09/2005 04:17 PM

Last Updated: 11/01/2010 12:00 PM



Health	2
Fire	1
Reactivity	0
Personal Protection	E

Material Safety Data Sheet

Terephthalic Acid MSDS

Section 1: Chemical Product and Company Identification

Product Name: Terephthalic Acid

Catalog Codes: SLT3019

CAS#: 100-21-0

RTECS: WZ0875000

TSCA: TSCA 8(b) inventory: Terephthalic Acid

CI#: Not available.

Synonym: 1,4-Benzenedicarboxylic Acid

Chemical Name: Terephthalic Acid

Chemical Formula: C8-H6-O4

Contact Information:

Sciencelab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396

US Sales: **1-800-901-7247**
International Sales: **1-281-441-4400**

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:
1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Terephthalic Acid	100-21-0	100

Toxicological Data on Ingredients: Terephthalic Acid: ORAL (LD50): Acute: 6400 mg/kg [Rat]. 3200 mg/kg [Mouse].

Section 3: Hazards Identification

Potential Acute Health Effects: Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation (lung irritant).

Potential Chronic Health Effects:
CARCINOGENIC EFFECTS: Classified None. by OSHA, None. by NIOSH. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. The substance is toxic to blood, kidneys, liver, bladder, brain, cardiovascular system, eyes, Nutritional and Gross Metabolic, ears, nose/sinuses, throat. Repeated or prolonged exposure to the substance can produce target organs damage.

Section 4: First Aid Measures

Eye Contact: Check for and remove any contact lenses. Do not use an eye ointment. Seek medical attention.

Skin Contact:

After contact with skin, wash immediately with plenty of water. Gently and thoroughly wash the contaminated skin with running water and non-abrasive soap. Be particularly careful to clean folds, crevices, creases and groin. Cover the irritated skin with an emollient. If irritation persists, seek medical attention. Wash contaminated clothing before reusing.

Serious Skin Contact:
Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek medical attention.

Inhalation: Allow the victim to rest in a well ventilated area. Seek immediate medical attention.

Serious Inhalation: Not available.

Ingestion:
Do not induce vomiting. Loosen tight clothing such as a collar, tie, belt or waistband. If the victim is not breathing, perform mouth-to-mouth resuscitation. Seek immediate medical attention.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: May be combustible at high temperature.

Auto-Ignition Temperature: 495°C (923°F)

Flash Points: OPEN CUP: 260°C (500°F).

Flammable Limits: Not available.

Products of Combustion: These products are carbon oxides (CO, CO2).

Fire Hazards in Presence of Various Substances: Not available.

Explosion Hazards in Presence of Various Substances:
Risks of explosion of the product in presence of mechanical impact: Not available. Risks of explosion of the product in presence of static discharge: Not available.

Fire Fighting Media and Instructions:
SMALL FIRE: Use DRY chemical powder. LARGE FIRE: Use water spray, fog or foam. Do not use water jet.

Special Remarks on Fire Hazards: Not available.

Special Remarks on Explosion Hazards: Not available.

Section 6: Accidental Release Measures

Small Spill:
Use appropriate tools to put the spilled solid in a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and dispose of according to local and regional authority requirements.

Large Spill:
Use a shovel to put the material into a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and allow to evacuate through the sanitary system. Be careful that the product is not present at a concentration level above TLV. Check TLV on the MSDS and with local authorities.

Section 7: Handling and Storage

Precautions:
Keep away from heat. Keep away from sources of ignition. Empty containers pose a fire risk, evaporate the residue under a fume hood. Ground all equipment containing material. Do not ingest. Do not breathe dust. Wear suitable protective clothing If ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes Keep away from incompatibles such as oxidizing agents.

Storage:

Keep container dry. Keep in a cool place. Ground all equipment containing material. Keep container tightly closed. Keep in a cool, well-ventilated place. Combustible materials should be stored away from extreme heat and away from strong oxidizing agents.

Section 8: Exposure Controls/Personal Protection

Engineering Controls:
Use process enclosures, local exhaust ventilation, or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fume or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.

Personal Protection:
Splash goggles. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.

Personal Protection in Case of a Large Spill:
Splash goggles. Full suit. Dust respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits:
TWA: 10 (mg/m3) from ACGIH (TLV) Consult local authorities for acceptable exposure limits.

Section 9: Physical and Chemical Properties

Physical state and appearance: Solid. (Powdered solid.)

Odor: Not available.

Taste: Not available.

Molecular Weight: 166.13 g/mole

Color: Off-white.

pH (1% soln/water): Not applicable.

Boiling Point: Not available.

Melting Point: 300°C (572°F)

Critical Temperature: Not available.

Specific Gravity: Not available.

Vapor Pressure: Not applicable.

Vapor Density: 5.74 (Air = 1)

Volatility: Not available.

Odor Threshold: Not available.

Water/Oil Dist. Coeff.: Not available.

Ionicity (in Water): Not available.

Dispersion Properties: Is not dispersed in cold water, hot water, methanol, diethyl ether, n-octanol, acetone.

Solubility: Insoluble in cold water, hot water, methanol, diethyl ether, n-octanol, acetone.

Section 10: Stability and Reactivity Data

Stability: The product is stable.

Instability Temperature: Not available.

Conditions of Instability: Not available.

Incompatibility with various substances: Reactive with oxidizing agents.

Corrosivity: Not available.

Special Remarks on Reactivity: Not available.

Special Remarks on Corrosivity: Not available.

Polymerization: No.

Section 11: Toxicological Information

Routes of Entry: Absorbed through skin. Dermal contact. Eye contact. Ingestion.

Toxicity to Animals: Acute oral toxicity (LD50): 3200 mg/kg [Mouse].

Chronic Effects on Humans:
CARCINOGENIC EFFECTS: Classified None. by OSHA, None. by NIOSH. The substance is toxic to blood, kidneys, liver, bladder, brain, cardiovascular system, eyes, Nutritional and Gross Metabolic, ears, nose/sinuses, throat.

Other Toxic Effects on Humans: Hazardous in case of skin contact (irritant), of ingestion, of inhalation (lung irritant).

Special Remarks on Toxicity to Animals: Not available.

Special Remarks on Chronic Effects on Humans: Not available.

Special Remarks on other Toxic Effects on Humans: Not available.

Section 12: Ecological Information

Ecotoxicity: Not available.

BOD5 and COD: Not available.

Products of Biodegradation:
Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

Toxicity of the Products of Biodegradation: The product itself and its products of degradation are not toxic.

Special Remarks on the Products of Biodegradation: Not available.

Section 13: Disposal Considerations

Waste Disposal:

Section 14: Transport Information

DOT Classification: Not a DOT controlled material (United States).

Identification: Not applicable.

Special Provisions for Transport: Not applicable.

Section 15: Other Regulatory Information

Federal and State Regulations:
California prop. 65 (no significant risk level): Terephthalic Acid Pennsylvania RTK: Terephthalic Acid Minnesota: Terephthalic Acid Massachusetts RTK: Terephthalic Acid New Jersey: Terephthalic Acid TSCA 8(b) inventory: Terephthalic Acid

Other Regulations: EINECS: This product is on the European Inventory of Existing Commercial Chemical Substances.

Other Classifications:

WHMIS (Canada): Not controlled under WHMIS (Canada).

DSCL (EEC):
R36/37/38- Irritating to eyes, respiratory system and skin.

HMIS (U.S.A.):

Health Hazard: 2

Fire Hazard: 1

Reactivity: 0

Personal Protection: E

National Fire Protection Association (U.S.A.):

Health: 0

Flammability: 1

Reactivity: 0

Specific hazard:

Protective Equipment:
Gloves. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Splash goggles.

Section 16: Other Information

References: Not available.

Other Special Considerations: Not available.

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MATERIAL SAFETY DATA SHEET

Date Printed: 05/24/2004
Date Updated: 03/07/2004
Version 1.3

Section 1 - Product and Company Information

Product Name	1,4-BUTANEDIOL, 99+%
Product Number	240559
Brand	ALDRICH
Company	Sigma-Aldrich
Street Address	3050 Spruce Street
City, State, Zip, Country	SAINT LOUIS MO 63103 US
Technical Phone:	314 771 5765
Emergency Phone:	414 273 3850 Ext. 5996
Fax:	800 325 5052

Section 2 - Composition/Information on Ingredient

Substance Name	CAS #	SARA 313
1,4-BUTANEDIOL	110-63-4	No

Formula	$C_4H_{10}O_2$
Synonyms	Agrisynth B1D * Butanediol * Butane-1,4-diol * 1,4-Butylene glycol * 1,4-Dihydroxybutane * DIOL 14B * Sucol B * Tetramethylene 1,4-diol * 1,4-Tetramethylene glycol
RTECS Number:	EK0525000

Section 3 - Hazards Identification

EMERGENCY OVERVIEW
Harmful.
Harmful if swallowed.
Target organ(s): Kidneys. Central nervous system.

HMIS RATING
HEALTH: 1*
FLAMMABILITY: 0
REACTIVITY: 0

NFPA RATING
HEALTH: 1
FLAMMABILITY: 0
REACTIVITY: 0

*additional chronic hazards present.

For additional information on toxicity, please refer to Section 11.

Section 4 - First Aid Measures

ORAL EXPOSURE
If swallowed, wash out mouth with water provided person is conscious. Call a physician.

INHALATION EXPOSURE

If inhaled, remove to fresh air. If not breathing give artificial respiration. If breathing is difficult, give oxygen.

DERMAL EXPOSURE

In case of skin contact, flush with copious amounts of water for at least 15 minutes. Remove contaminated clothing and shoes. Call a physician.

EYE EXPOSURE

In case of contact with eyes, flush with copious amounts of water for at least 15 minutes. Assure adequate flushing by separating the eyelids with fingers. Call a physician.

Section 5 - Fire Fighting Measures

FLASH POINT

273.2 °F   134 °C   Method: closed cup

AUTOIGNITION TEMP

370 °C

FLAMMABILITY

N/A

EXTINGUISHING MEDIA

Suitable: Carbon dioxide, dry chemical powder, or appropriate foam. Water spray.

FIREFIGHTING

Protective Equipment: Wear self-contained breathing apparatus and protective clothing to prevent contact with skin and eyes.
Specific Hazard(s): Emits toxic fumes under fire conditions.

Section 6 - Accidental Release Measures

PROCEDURE TO BE FOLLOWED IN CASE OF LEAK OR SPILL

Evacuate area.

PROCEDURE(S) OF PERSONAL PRECAUTION(S)

Wear self-contained breathing apparatus, rubber boots, and heavy rubber gloves.

METHODS FOR CLEANING UP

Absorb on sand or vermiculite and place in closed containers for disposal. Ventilate area and wash spill site after material pickup is complete.

Section 7 - Handling and Storage

HANDLING

User Exposure: Avoid prolonged or repeated exposure. Do not breathe vapor. Avoid contact with eyes, skin, and clothing.

STORAGE

Suitable: Keep tightly closed.

Section 8 - Exposure Controls / PPE

ENGINEERING CONTROLS

Safety shower and eye bath. Mechanical exhaust required.

PERSONAL PROTECTIVE EQUIPMENT

Respiratory: Government approved respirator.
Hand: Compatible chemical-resistant gloves.
Eye: Chemical safety goggles.

GENERAL HYGIENE MEASURES

Wash thoroughly after handling.

Section 9 - Physical/Chemical Properties

Appearance	Physical State: Liquid	
Property	**Value**	**At Temperature or Pressure**
Molecular Weight	90.12 AMU	
pH	N/A	
BP/BP Range	120 - 122 ˚C	10 mmHg
MP/MP Range	19 ˚C	
Freezing Point	N/A	
Vapor Pressure	N/A	
Vapor Density	3.1 g/l	
Saturated Vapor Conc.	N/A	
SG/Density	1.014 g/cm3	
Bulk Density	N/A	
Odor Threshold	N/A	
Volatile%	N/A	
VOC Content	N/A	
Water Content	N/A	
Solvent Content	N/A	
Evaporation Rate	N/A	
Viscosity	N/A	
Surface Tension	N/A	
Partition Coefficient	N/A	
Decomposition Temp.	N/A	
Flash Point	273.2 ˚F 134 ˚C	Method: closed cup
Explosion Limits	N/A	
Flammability	N/A	
Autoignition Temp	370 ˚C	
Refractive Index	1.446	
Optical Rotation	N/A	
Miscellaneous Data	N/A	
Solubility	N/A	

N/A = not available

Section 10 - Stability and Reactivity

STABILITY

Stable: Stable.
Materials to Avoid: Strong oxidizing agents, Acid chlorides, Acid anhydrides, Reducing agents.

HAZARDOUS DECOMPOSITION PRODUCTS

Hazardous Decomposition Products: Carbon monoxide, Carbon dioxide.

HAZARDOUS POLYMERIZATION

Hazardous Polymerization: Will not occur

Section 11 - Toxicological Information

ROUTE OF EXPOSURE

Skin Contact: May cause skin irritation.
Skin Absorption: May be harmful if absorbed through the skin.

Eye Contact: May cause eye irritation.
Inhalation: Material may be irritating to mucous membranes and upper respiratory tract. May be harmful if inhaled.
Ingestion: Harmful if swallowed.

TARGET ORGAN(S) OR SYSTEM(S)
Kidneys. Central nervous system.

SIGNS AND SYMPTOMS OF EXPOSURE
To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

TOXICITY DATA

Rectal
Man
429 MG/KG
LDLO

Oral
Rat
1525 mg/kg
LD50
Remarks: Behavioral:Altered sleep time (including change in righting reflex). Behavioral:Somnolence (general depressed activity). Blood:Other changes.

Intraperitoneal
Rat
1070 MG/KG
LD50

Oral
Mouse
2062 mg/kg
LD50
Remarks: Behavioral:Altered sleep time (including change in righting reflex). Behavioral:Somnolence (general depressed activity). Blood:Other changes.

Intraperitoneal
Mouse
1650 MG/KG
LD50

Oral
Rabbit
2531 mg/kg
LD50
Remarks: Behavioral:Altered sleep time (including change in righting reflex). Behavioral:Somnolence (general depressed activity). Blood:Other changes.

Oral
Guinea pig
1200 mg/kg
LD50
Remarks: Behavioral:Altered sleep time (including change in righting reflex). Behavioral:Somnolence (general depressed activity). Blood:Other changes.

Section 12 - Ecological Information

Section 13 - Disposal Considerations

APPROPRIATE METHOD OF DISPOSAL OF SUBSTANCE OR PREPARATION

Contact a licensed professional waste disposal service to dispose of this material. Dissolve or mix the material with a combustible solvent and burn in a chemical incinerator equipped with an afterburner and scrubber. Observe all federal, state, and local environmental regulations.

Section 14 - Transport Information

DOT

Proper Shipping Name: None

Non-Hazardous for Transport: This substance is considered to be non-hazardous for transport.

IATA

Non-Hazardous for Air Transport: Non-hazardous for air transport.

Section 15 - Regulatory Information

EU ADDITIONAL CLASSIFICATION

Symbol of Danger: Xn
Indication of Danger: Harmful.
R: 22
Risk Statements: Harmful if swallowed.
S: 36
Safety Statements: Wear suitable protective clothing.

US CLASSIFICATION AND LABEL TEXT

Indication of Danger: Harmful.
Risk Statements: Harmful if swallowed.
Safety Statements: Wear suitable protective clothing.
US Statements: Target organ(s): Kidneys. Central nervous system.

UNITED STATES REGULATORY INFORMATION

SARA LISTED: No
TSCA INVENTORY ITEM: Yes

CANADA REGULATORY INFORMATION

WHMIS Classification: This product has been classified in accordance with the hazard criteria of the CPR, and the MSDS contains all the information required by the CPR.

DSL: Yes
NDSL: No

Section 16 - Other Information

DISCLAIMER

For R&D use only. Not for drug, household or other uses.

WARRANTY

The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Inc., shall not be held liable for any damage resulting from handling or from contact with the above product. See reverse side of invoice or packing slip for additional terms and conditions of sale.

American International Chemical, Inc.
Corporate Offices: (800) 238-0001
Internet: www.aicma.com *Email:* info@aicma.com

MATERIAL SAFETY DATA SHEET

ERUCAMIDE

SECTION 1 - CHEMICAL PRODUCT AND COMPANY INFORMATION

American International Chemical, Inc.	**Emergency Number: Chemtrec**	**800-424-9300**
135 Newbury Street		**703-527-3887**
Framingham, MA 01701	**Information Number:**	**800-238-0001**

Date: August 2007

Synonyms: Erucamide

CAS #: 112-84-5

DOT Hazard Class: Not Regulated

SECTION 2 - COMPOSITION AND INFORMATION ON INGREDIENTS

Erucamide	80% min.
Mixed fatty amides	20% max.

SECTION 3 - HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW: A white bead or powder that presents little or no health hazard and no unusual hazard if involved in a fire.

POTENTIAL HEALTH EFFECTS:
Skin: Wash skin thoroughly with soap and water for at least 15 minutes.
Eyes: Immediately flush eyes with water for at least 15 minutes.
Inhalation: Remove to fresh air.
Ingestion: Molten product can cause thermal burns. Obtain immediate medical attention.
CARCINOGENICITY: Not Identifiable

SECTION 4 - FIRST AID MEASURES

Skin: Immediately wash skin with soap and water for at least 15 minutes. If redness or irritation occurs, seek medical attention.
Eyes: Immediately flush eyes with plenty of water for at least 15 minutes. If redness or irritation occurs, seek medical attention.
Inhalation: Remove to the fresh air.
Ingestion: Wash out mouth with water. Molten product can cause thermal burns. Obtain immediate medical attention
On All Of The Above: Consult a physician if symptoms persist.

SECTION 5 - FIRE FIGHTING MEASURES

Flash Point: 220 °C (428 °F)

Flammable Limits: Non Combustible

Extinguishing Media: Use media that is appropriate to treat surrounding fire.

Special Fire Fighting Procedures:
Use fire fighting procedure that is appropriate to treat surrounding fire. All firefighters should use self-contained breathing apparatus and full fire-fighting turn-out gear.

Unusual Fire Explosion Hazard: During a fire, irritating and highly toxic gasses may be generated by thermal decomposition or combustion.

Auto Ignition Temperature: Not Applicable

SECTION 6 - ACCIDENTAL RELEASE MEASURES

Isolate hazard area and deny entry to unnecessary or unprotected personnel.
Contain spill, sweep up, collect and place in a disposal container. Avoid runoff into storm sewers and ditches which lead to waterways.

SECTION 7 - HANDLING AND STORAGE

Avoid contact with skin, eyes and clothing. Use with adequate ventilation. Avoid breathing dust. Use normal personal hygiene and housekeeping. Store in cool dry area away from other incompatible materials. Product is slightly hygroscopic and should be stored in a dry area to prevent moisture pick up and caking.

SECTION 8 - EXPOSURE CONTROLS, PERSONAL PROTECTION

RESPIRATORY PROTECTION: Use NIOSH/MSHA approved respirators.

VENTILATION REQUIREMENTS: Ventilate as necessary to eliminate dust from the work area and maintain concentrations below the limit.

SKIN AND EYE PROTECTION: Use rubber or neoprene gloves, chemical goggles and clothing sufficient to protect skin and eyes from dust.

WORK, HYGIENIC PRACTICES:
As required to protect skin and eyes from dust, safety showers and/or eye wash should be available. Do not leave food or smoke in work area. Wash thoroughly and remove or clean any contaminated clothing.

EXPOSURE LIMITS: None Established

SECTION 9 - PHYSICAL AND CHEMICAL PROPERTIES

Boiling Point: > 287 °C (>550 °F)

Vapor Pressure (MM Hg): Negligible

Vapor Density (AIR=1): Negligible

Specific Gravity ($H_20=1$): approx. 0.88 g/cm3 at 25 °C

Percent Volatile by Volume (%): Not Applicable

Melting Point: 83 +/- 5 °C

Evaporation Rate (Butyl Acetate=1): Not Applicable

Solubility in Water: Insoluble

pH: Not Applicable

SECTION 10 - STABILITY AND REACTIVITY

CHEMICAL STABILITY: Stable under normal temperatures and pressures.

HAZARDOUS POLYMERIZATION: Will not occur under normal conditions.

HAZARDOUS DECOMPOSITION PRODUCTS: Burning can produce carbon monoxide, carbon dioxide and oxides of nitrogen.

KEEP AWAY FROM: Strong oxidizing agents.

SECTION 11 - TOXICOLOGICAL INFORMATION

Not Available

SECTION 12 - ECOLOGICAL INFORMATION

Not Available

SECTION 13 - DISPOSAL CONSIDERATIONS

Dispose of in accordance with all federal, state and local regulations.

RCRA WASTE #: Not Listed

SECTION 14 - TRANSPORTATION INFORMATION

D.O.T. SHIPPING NAME: ERUCAMIDE - Not Regulated

SECTION 15 - REGULATORY INFORMATION

OSHA STATUS: Not listed

TSCA STATUS: Listed

CERCLA REPORTABLE REQUIREMENTS: (RQ) None

SARA TITLE III INFORMATION:
Section 302 Extremely Hazardous Substance Not listed

Section 313 Toxic Chemicals: Not listed

Section 311/312 Hazard Category: Not considered a hazard.

SECTION 16 - OTHER INFORMATION

HMIS Ratings: Health =1 Flammability = 1 Reactivity = 0

Reason for Issue: Changed Date

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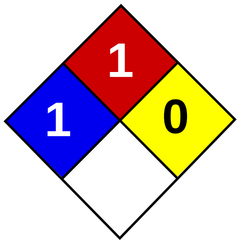

Health	1
Fire	1
Reactivity	0
Personal Protection	G

Material Safety Data Sheet

Glycerin MSDS

Section 1: Chemical Product and Company Identification

Product Name: Glycerin

Catalog Codes: SLG1171, SLG1894, SLG1111, SLG1615

CAS#: 56-81-5

RTECS: MA8050000

TSCA: TSCA 8(b) inventory: Glycerin

CI#: Not available.

Synonym: 1,2,3-Propanetriol; Glycerol

Chemical Name: Glycerin

Chemical Formula: $C_3H_5(OH)_3$

Contact Information:

Sciencelab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396

US Sales: **1-800-901-7247**
International Sales: **1-281-441-4400**

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:
1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Glycerin	56-81-5	100

Toxicological Data on Ingredients: Glycerin: ORAL (LD50): Acute: 12600 mg/kg [Rat]. 4090 mg/kg [Mouse]. DERMAL (LD50): Acute: 10000 mg/kg [Rabbit]. MIST(LC50): Acute: >570 mg/m 1 hours [Rat].

Section 3: Hazards Identification

Potential Acute Health Effects: Slightly hazardous in case of skin contact (irritant, permeator), of eye contact (irritant), of ingestion, of inhalation.

Potential Chronic Health Effects:
CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. The substance may be toxic to kidneys. Repeated or prolonged exposure to the substance can produce target organs damage.

Section 4: First Aid Measures

Eye Contact:
Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention if irritation occurs.

Skin Contact:
Wash with soap and water. Cover the irritated skin with an emollient. Get medical attention if irritation develops. Cold water may be used.

Serious Skin Contact: Not available.

Inhalation:
If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention immediately.

Serious Inhalation: Not available.

Ingestion:
Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention if symptoms appear.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: May be combustible at high temperature.

Auto-Ignition Temperature:
370°C (698°F)(NFPA Fire Protection Guide to Hazardous Materials, 13th ed., 2002; NIOSH ICSC, 2001; CHRIS, 2001) 392 C (739 F) (Lewis, 1997)

Flash Points:
CLOSED CUP: 160°C (320°F). (Chemical Hazard Response Information System, 2001; Lewis, 1997). OPEN CUP: 177°C (350.6°F) (Budavari, 2000; Chemical Response Information System, 2001; NIOSH ICSC, 2001) OPEN CUP: 199 C(390 F) (National Fire Protection Association, Fire Protection Guide to Hazardous Materials, 13 ed., 2002)

Flammable Limits: LOWER: 0.9%

Products of Combustion: These products are carbon oxides (CO, CO2), irritating and toxic fumes.

Fire Hazards in Presence of Various Substances:
Slightly flammable to flammable in presence of open flames and sparks, of heat, of oxidizing materials. Non-flammable in presence of shocks.

Explosion Hazards in Presence of Various Substances:
Risks of explosion of the product in presence of mechanical impact: Not available. Risks of explosion of the product in presence of static discharge: Not available. Explosive in presence of oxidizing materials.

Fire Fighting Media and Instructions:
SMALL FIRE: Use DRY chemical powder. LARGE FIRE: Use water spray, fog or foam. Do not use water jet.

Special Remarks on Fire Hazards: Not available.

Special Remarks on Explosion Hazards:
Glycerin is incompatible with strong oxidizers such as chromium trioxide, potassium chlorate, or potassium permanganate and may explode on contact with these compounds. Explosive glyceryl nitrate is formed from a mixture of glycerin and nitric and sulfuric acids. Perchloric acid , lead oxide + glycerin form perchloric esters which may be explosive. Glycerin and chlorine may explode if heated and confined.

Section 6: Accidental Release Measures

Small Spill:
Dilute with water and mop up, or absorb with an inert dry material and place in an appropriate waste disposal container. Finish cleaning by spreading water on the contaminated surface and dispose of according to local and regional authority requirements.

Large Spill:

Stop leak if without risk. If the product is in its solid form: Use a shovel to put the material into a convenient waste disposal container. If the product is in its liquid form: Do not get water inside container. Absorb with an inert material and put the spilled material in an appropriate waste disposal. Do not touch spilled material. Use water spray to reduce vapors. Prevent entry into sewers, basements or confined areas; dike if needed. Eliminate all ignition sources. Call for assistance on disposal. Finish cleaning by spreading water on the contaminated surface and allow to evacuate through the sanitary system. Be careful that the product is not present at a concentration level above TLV. Check TLV on the MSDS and with local authorities.

Section 7: Handling and Storage

Precautions:
Keep away from heat. Keep away from sources of ignition. Ground all equipment containing material. Do not ingest. Do not breathe gas/fumes/ vapor/spray. Wear suitable protective clothing. If ingested, seek medical advice immediately and show the container or the label. Keep away from incompatibles such as oxidizing agents.

Storage: Keep container tightly closed. Keep container in a cool, well-ventilated area. Hygroscopic

Section 8: Exposure Controls/Personal Protection

Engineering Controls:
Provide exhaust ventilation or other engineering controls to keep the airborne concentrations of vapors below their respective threshold limit value. Ensure that eyewash stations and safety showers are proximal to the work-station location.

Personal Protection:
Safety glasses. Lab coat. Vapor respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.

Personal Protection in Case of a Large Spill:
Splash goggles. Full suit. Vapor respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits:
TWA: 10 (mg/m3) from ACGIH (TLV) [United States] [1999] Inhalation Total. TWA: 15 (mg/m3) from OSHA (PEL) [United States] Inhalation Total. TWA: 10 STEL: 20 (mg/m3) [Canada] TWA: 5 (mg/m3) from OSHA (PEL) [United States] Inhalation Respirable.Consult local authorities for acceptable exposure limits.

Section 9: Physical and Chemical Properties

Physical state and appearance: Liquid. (Viscous (Syrupy) liquid.)

Odor: Mild

Taste: Sweet.

Molecular Weight: 92.09 g/mole

Color: Clear Colorless.

pH (1% soln/water): Not available.

Boiling Point: 290°C (554°F)

Melting Point: 19°C (66.2°F)

Critical Temperature: Not available.

Specific Gravity: 1.2636 (Water = 1)

Vapor Pressure: 0 kPa (@ 20°C)

Vapor Density: 3.17 (Air = 1)

Volatility: Not available.

Odor Threshold: Not available.

Water/Oil Dist. Coeff.: The product is more soluble in water; log(oil/water) = -1.8

Ionicity (in Water): Not available.

Dispersion Properties: See solubility in water, acetone.

Solubility:
Miscible in cold water, hot water and alcohol. Partially soluble in acetone. Very slightly soluble in diethyl ether (ethyl ether). Limited solubility in ethyl acetate. Insoluble in carbon tetrachloride, benzene, chloroform, petroleum ethers, and oils

Section 10: Stability and Reactivity Data

Stability: The product is stable.

Instability Temperature: Not available.

Conditions of Instability: Avoid contact with incompatible materials, excess heat and ignition, sources, moisture.

Incompatibility with various substances: Highly reactive with oxidizing agents.

Corrosivity: Non-corrosive in presence of glass.

Special Remarks on Reactivity:
Hygroscopic. Glycerin is incompatible with strong oxidizers such as chromium trioxide, potassium chlorate, or potassium permanganate. Glycerin may react violently with acetic anhydride, aniline and nitrobenzene, chromic oxide, lead oxide and fluorine, phosphorous triiodide, ethylene oxide and heat, silver perchlorate, sodium peroxide, sodium hydride.

Special Remarks on Corrosivity: Not available.

Polymerization: Will not occur.

Section 11: Toxicological Information

Routes of Entry: Absorbed through skin. Eye contact.

Toxicity to Animals:
WARNING: THE LC50 VALUES HEREUNDER ARE ESTIMATED ON THE BASIS OF A 4-HOUR EXPOSURE. Acute oral toxicity (LD50): 4090 mg/kg [Mouse]. Acute dermal toxicity (LD50): 10000 mg/kg [Rabbit]. Acute toxicity of the mist (LC50): >570 mg/m3 1 hours [Rat].

Chronic Effects on Humans: May cause damage to the following organs: kidneys.

Other Toxic Effects on Humans: Slightly hazardous in case of skin contact (irritant), of ingestion, of inhalation.

Special Remarks on Toxicity to Animals:
TDL (rat) - Route: Oral; Dose: 100 mg/kg 1 day prior to mating. TDL (human) - Route: Oral; Dose: 1428 mg/kg

Special Remarks on Chronic Effects on Humans:
Glycerin is transferred across the plancenta in small amounts. May cause adverse reproductive effects based on animal data (Paternal Effects (Rat): Spermatogenesis (including genetic material, sperm morphology, motility, and count), Testes, epididymis, sperm duct). May affect genetic material.

Special Remarks on other Toxic Effects on Humans:
Acute Potential Health Effects: Low hazard for normal industrial handling or normal workplace conditions. Skin: May cause skin irritation. May be absorbed through skin Eyes: May cause eye irritation with stinging, redness, burning sensation, and tearing, but no eye injury. Ingestion: Low hazard. Low toxicity except with very large doses. When large doses are ingested, it can cause gastrointestinal tract irritation with thirst (dehydration), nausea or vomiting diarrhea. It may also affect behavior/central nervous system/nervous system (central nervous system depression, general anesthetic, headache, dizziness, confusion, insomnia, toxic psychosis, muscle weakness, paralysisconvulsions), urinary system/kidneys(renal failure,

hemoglobinuria), cardiovascular system (cardiac arrhythmias), liver. It may also cause elevated blood sugar. Inhalation: Due to low vapor pressure, inhalation of the vapors at room temperature is unlikely. Inhalation of mist may cause respiratory tract irritation. Chronic Potential Health Effects: Ingestion: Prolonged or repeated ingestion may affect the blood(hemolysis, changes in white blood cell count), endocrine system (changes in adrenal weight), respiratory system, and may cause kidney injury.

Section 12: Ecological Information

Ecotoxicity: Ecotoxicity in water (LC50): 58.5 ppm 96 hours [Trout].

BOD5 and COD: Not available.

Products of Biodegradation:
Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

Toxicity of the Products of Biodegradation: The products of degradation are less toxic than the product itself.

Special Remarks on the Products of Biodegradation: Not available.

Section 13: Disposal Considerations

Waste Disposal:
Waste must be disposed of in accordance with federal, state and local environmental control regulations.

Section 14: Transport Information

DOT Classification: Not a DOT controlled material (United States).

Identification: Not applicable.

Special Provisions for Transport: Not applicable.

Section 15: Other Regulatory Information

Federal and State Regulations:
Illinois toxic substances disclosure to employee act: Glycerin Rhode Island RTK hazardous substances: Glycerin Pennsylvania RTK: Glycerin Minnesota: Glycerin Massachusetts RTK: Glycerin Tennessee - Hazardous Right to Know: Glycerin TSCA 8(b) inventory: Glycerin

Other Regulations:
OSHA: Hazardous by definition of Hazard Communication Standard (29 CFR 1910.1200). EINECS: This product is on the European Inventory of Existing Commercial Chemical Substances.

Other Classifications:

WHMIS (Canada): Not controlled under WHMIS (Canada).

DSCL (EEC):
Not available S24/25- Avoid contact with skin and eyes.

HMIS (U.S.A.):

Health Hazard: 1

Fire Hazard: 1

Reactivity: 0

Personal Protection: g

National Fire Protection Association (U.S.A.):

Health: 1

Flammability: 1

Reactivity: 0

Specific hazard:

Protective Equipment:
Gloves. Lab coat. Vapor respirator. Be sure to use an approved/certified respirator or equivalent. Wear appropriate respirator when ventilation is inadequate. Safety glasses.

Section 16: Other Information

References: Not available.

Other Special Considerations: Not available.

Created: 10/10/2005 08:38 PM

Last Updated: 11/01/2010 12:00 PM

American International Chemical, Inc.
Corporate Offices: (800) 238-0001
Internet: www.aicma.com *Email:* info@aicma.com

MATERIAL SAFETY DATA SHEET

STEARAMIDE

SECTION 1 - CHEMICAL PRODUCT AND COMPANY INFORMATION

American International Chemical, Inc.	**Emergency Number: Chemtrec**	**800-424-9300**
135 Newbury Street		**703-527-3887**
Framingham, MA 01701	**Information Number:**	**800-238-0001**

Date: August 2007

Synonyms: Stearamide

CAS #: 124-26-5

DOT Hazard Class: Not Regulated

SECTION 2 - COMPOSITION AND INFORMATION ON INGREDIENTS

Stearamide	35% min.
Mixed fatty amides	65% max.

SECTION 3 - HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW: A white bead or powder that presents little or no health hazard and no unusual hazard if involved in a fire. Avoid dusting and all possible sources of ignition (spark or flame), as possibility of explosion exists under dusty conditions.

POTENTIAL HEALTH EFFECTS:
Skin: Wash skin thoroughly with soap and water for at least 15 minutes.
Eyes: Immediately flush eyes with water for at least 15 minutes.
Inhalation: Remove to fresh air.
Ingestion: Molten product can cause thermal burns – obtain immediate medical attention.
CARCINOGENICITY: Not Identifiable

SECTION 4 - FIRST AID MEASURES

Skin: Immediately wash skin with soap and water for at least 15 minutes. If redness or irritation occurs, seek medical attention.
Eyes: Immediately flush eyes with plenty of water for at least 15 minutes. If redness or irritation occurs, seek medical attention.
Inhalation: Remove to the fresh air.
Ingestion: Wash out mouth with water. Molten product can cause thermal burns – obtain immediate medical attention
On All Of The Above: Consult a physician if symptoms persist.

SECTION 5 - FIRE FIGHTING MEASURES

Flash Point: 197 °C (387 °F)

Flammable Limits: Non Combustible

Extinguishing Media: Use media that is appropriate to treat surrounding fire.

Special Fire Fighting Procedures:
Use fire fighting procedure that is appropriate to treat surrounding fire. All firefighters should use self-contained breathing apparatus and full fire-fighting turn-out gear.

Unusual Fire Explosion Hazard: During a fire, irritating and highly toxic gasses may be generated by thermal decomposition or combustion.

Auto Ignition Temperature: Not Applicable

SECTION 6 - ACCIDENTAL RELEASE MEASURES

Isolate hazard area and deny entry to unnecessary or unprotected personnel.
Contain spill, sweep up, collect and place in a disposal container. Avoid runoff into storm sewers and ditches which lead to waterways.

SECTION 7 - HANDLING AND STORAGE

Avoid contact with skin, eyes and clothing. Use with adequate ventilation. Avoid breathing dust. Use normal personal hygiene and housekeeping. Store in cool dry area away from other incompatible materials. Product is slightly hygroscopic and should be stored in a dry area to prevent moisture pick up and caking.

SECTION 8 - EXPOSURE CONTROLS, PERSONAL PROTECTION

RESPIRATORY PROTECTION: Use NIOSH/MSHA approved respirators.

VENTILATION REQUIREMENTS: Ventilate as necessary to eliminate dust from the work area and maintain concentrations below the limit.

SKIN AND EYE PROTECTION: Use rubber or neoprene gloves, chemical goggles and clothing sufficient to protect skin and eyes from dust.

WORK, HYGIENIC PRACTICES:
As required to protect skin and eyes from dust, safety showers and/or eye wash should be available. Do not leave food or smoke in work area. Wash thoroughly and remove or clean any contaminated clothing.

EXPOSURE LIMITS: None Established

SECTION 9 - PHYSICAL AND CHEMICAL PROPERTIES

Boiling Point: Not Applicable

Vapor Pressure (MM Hg): Negligible

Vapor Density (AIR=1): Negligible

Specific Gravity ($H_20=1$): approx. 0.885 g/cm3 at 25 °C

Percent Volatile by Volume (%): Not Applicable

Melting Point: 100 +/- 5 °C

Evaporation Rate (Butyl Acetate=1): Not Applicable

Solubility in Water: Insoluble

pH: Not Applicable

SECTION 10 - STABILITY AND REACTIVITY

CHEMICAL STABILITY: Stable under normal temperatures and pressures.

HAZARDOUS POLYMERIZATION: Will not occur under normal conditions.

HAZARDOUS DECOMPOSITION PRODUCTS: Burning can produce carbon monoxide, carbon dioxide and oxides of nitrogen.

KEEP AWAY FROM: Strong oxidizing agents.

SECTION 11 - TOXICOLOGICAL INFORMATION

Acute Oral Toxicity
LD50, Rat = 10,000 mg per kg body weight

SECTION 12 - ECOLOGICAL INFORMATION

Not Available

SECTION 13 - DISPOSAL CONSIDERATIONS

Dispose of in accordance with all federal, state and local regulations.

RCRA WASTE #: Not Listed

SECTION 14 - TRANSPORTATION INFORMATION

D.O.T. SHIPPING NAME: STEARAMIDE

SECTION 15 - REGULATORY INFORMATION

OSHA STATUS: Not listed

TSCA STATUS: Listed

CERCLA REPORTABLE REQUIREMENTS: (RQ) None

SARA TITLE III INFORMATION:

Section 302 Extremely Hazardous Substance: Not listed

Section 313 Toxic Chemicals: Not listed

Section 311/312 Hazard Category: Not considered a hazard.

SECTION 16 - OTHER INFORMATION

HMIS Ratings: Health =1 Flammability = 1 Reactivity = 0

Reason for Issue: Changed Date

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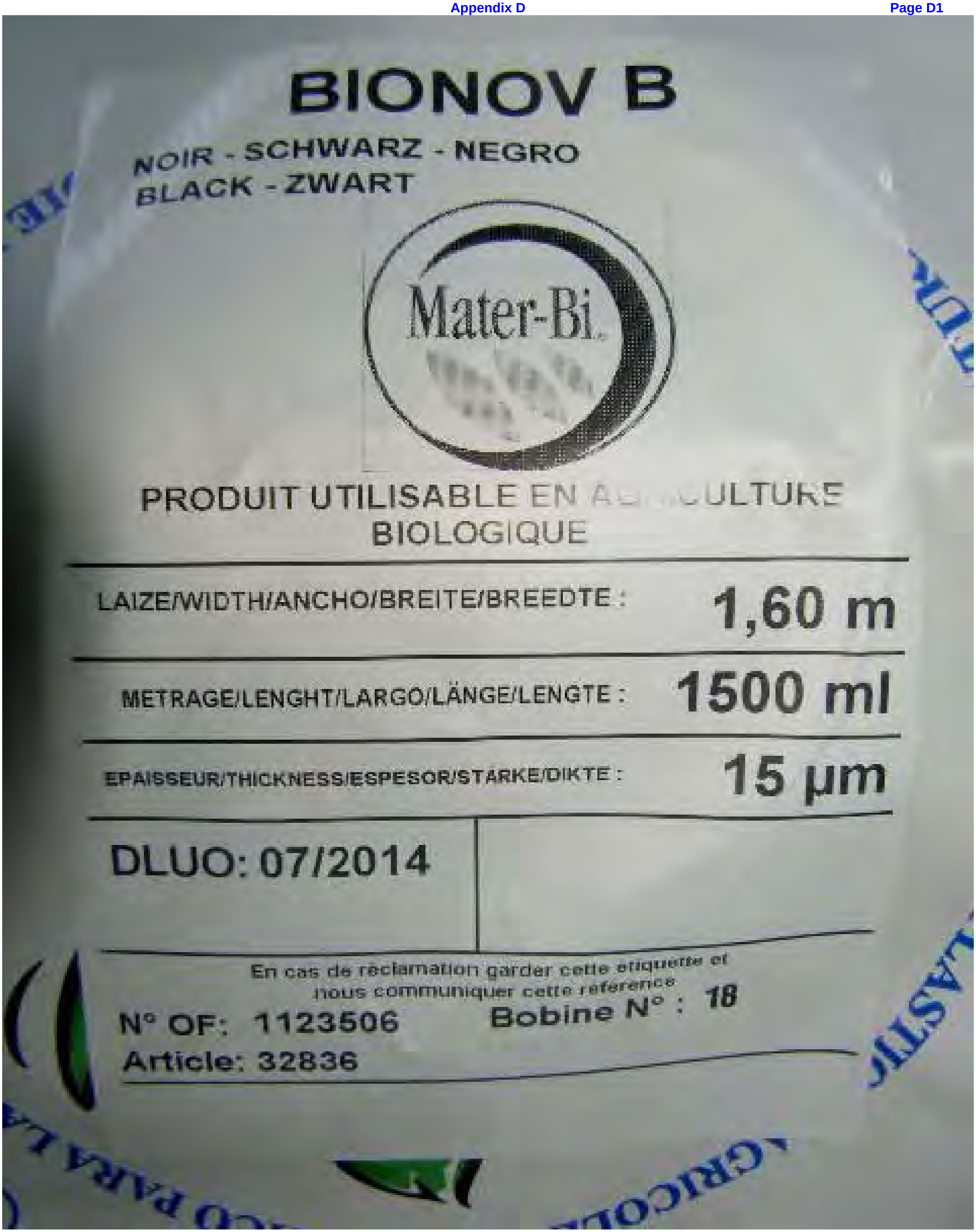


BIONOV B

NOIR - SCHWARZ - NEGRO
BLACK - ZWART

Mater-Bi

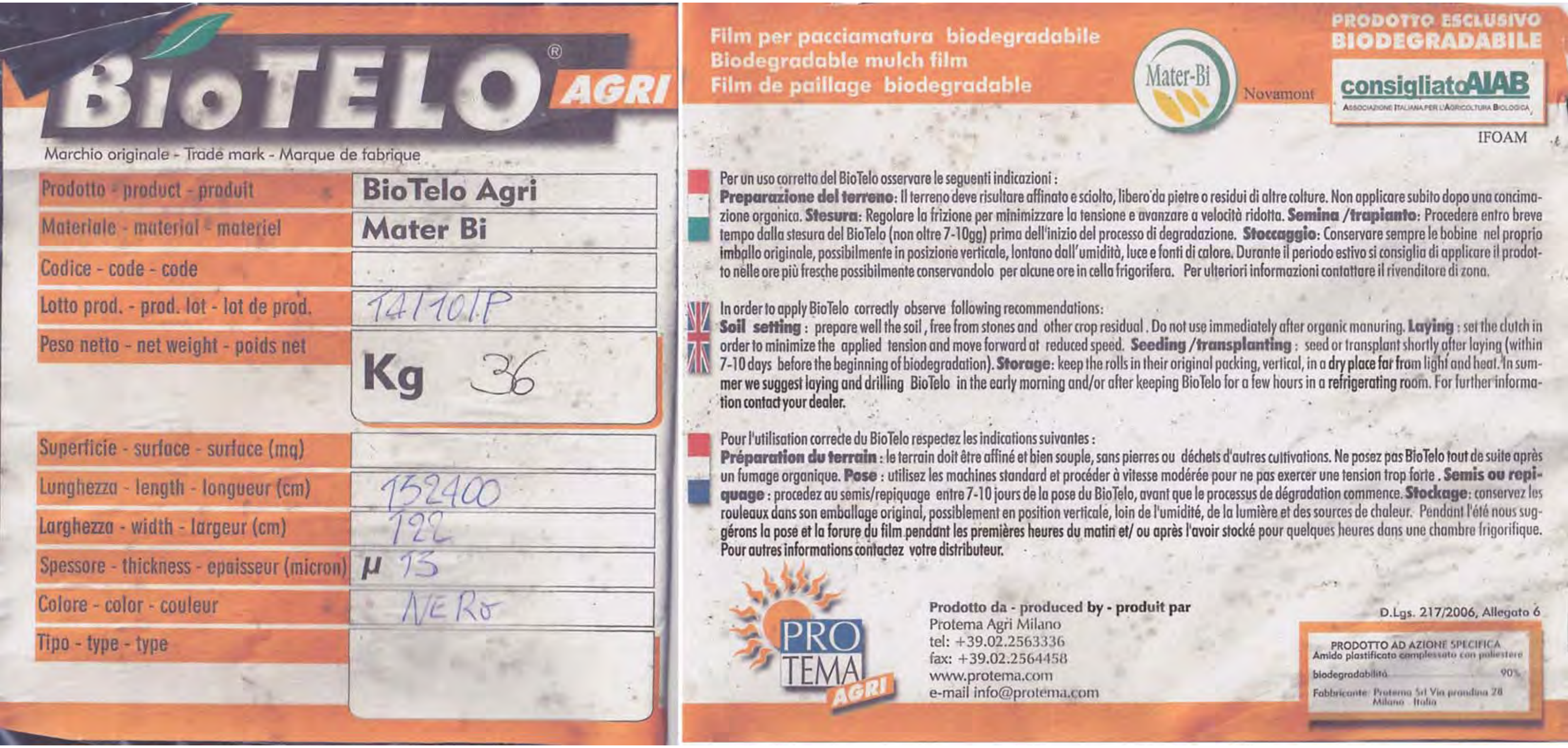
PRODUIT UTILISABLE EN AGRICULTURE
BIOLOGIQUE

LAIZE/WIDTH/ANCHO/BREITE/BREEDTE :	1,60 m
METRAGE/LENGHT/LARGO/LÄNGE/LENGTE :	1500 ml
EPAISSEUR/THICKNESS/ESPESOR/STARKE/DIKTE :	15 µm

DLUO: 07/2014

En cas de réclamation garder cette étiquette et
nous communiquer cette référence

N° OF: 1123506 Bobine N° : 18
Article: 32836



BioTELO® AGRI

Marchio originale - Trade mark - Marque de fabrique

Prodotto - product - produit	BioTelo Agri
Materiale - material - materiel	Mater Bi
Codice - code - code	
Lotto prod. - prod. lot - lot de prod.	14/10/P
Peso netto - net weight - poids net	Kg 36
Superficie - surface - surface (mq)	
Lunghezza - length - longueur (cm)	132400
Larghezza - width - largeur (cm)	122
Spessore - thickness - epaisseur (micron)	µ 13
Colore - color - couleur	NERo
Tipo - type - type	

Film per pacciamatura biodegradabile
Biodegradable mulch film
Film de paillage biodegradable

Mater-Bi

Novamont

PRODOTTO ESCLUSIVO BIODEGRADABILE

consigliato AIAB
Associazione Italiana per l'Agricoltura Biologica

IFOAM

Per un uso corretto del BioTelo osservare le seguenti indicazioni:
Preparazione del terreno: Il terreno deve risultare affinato e sciolto, libero da pietre o residui di altre colture. Non applicare subito dopo una concimazione organica. **Stesura**: Regolare la frizione per minimizzare la tensione e avanzare a velocità ridotta. **Semina /trapianto**: Procedere entro breve tempo dalla stesura del BioTelo (non oltre 7-10gg) prima dell'inizio del processo di degradazione. **Stoccaggio**: Conservare sempre le bobine nel proprio imballo originale, possibilmente in posizione verticale, lontano dall'umidità, luce e fonti di calore. Durante il periodo estivo si consiglia di applicare il prodotto nelle ore più fresche possibilmente conservandolo per alcune ore in cella frigorifera. Per ulteriori informazioni contattare il rivenditore di zona.

In order to apply BioTelo correctly observe following recommendations:
Soil setting: prepare well the soil, free from stones and other crop residual. Do not use immediately after organic manuring. **Laying**: set the clutch in order to minimize the applied tension and move forward at reduced speed. **Seeding /transplanting**: seed or transplant shortly after laying (within 7-10 days before the beginning of biodegradation). **Storage**: keep the rolls in their original packing, vertical, in a dry place far from light and heat. In summer we suggest laying and drilling BioTelo in the early morning and/or after keeping BioTelo for a few hours in a refrigerating room. For further information contact your dealer.

Pour l'utilisation correcte du BioTelo respectez les indications suivantes:
Préparation du terrain: le terrain doit être affiné et bien souple, sans pierres ou déchets d'autres cultivations. Ne posez pas BioTelo tout de suite après un fumage organique. **Pose**: utilisez les machines standard et procéder à vitesse modérée pour ne pas exercer une tension trop forte. **Semis ou repiquage**: procedez au semis/repiquage entre 7-10 jours de la pose du BioTelo, avant que le processus de dégradation commence. **Stockage**: conservez les rouleaux dans son emballage original, possiblement en position verticale, loin de l'umidité, de la lumière et des sources de chaleur. Pendant l'été nous suggérons la pose et la forure du film pendant les premières heures du matin et/ ou après l'avoir stocké pour quelques heures dans une chambre frigorifique. Pour autres informations contactez votre distributeur.

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Protema Agri Milano
tel: +39.02.2563336
fax: +39.02.2564458
www.protema.com
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D.Lgs. 217/2006, Allegato 6

PRODOTTO AD AZIONE SPECIFICA
Amido plastificato complessato con poliestere
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Milano Italia

A STUDY OF THE ACTION OF CARBON BLACK AND SIMILAR ABSORBING MATERIALS IN SOILS[1]

By

J. J. Skinner and J. H. Beattie, *Biochemists, Soil Fertility Investigations, U. S. Department of Agriculture*

Carbon black is a very good agent for purifying distilled water for plant physiological purposes, its action seeming to be one of absorbing substances of a solid or gaseous nature. It is used quite generally by plant physiologists in preparing good water for culture work. Other insoluble, finally divided materials, such as ferric hydrate, aluminum hydrate, magnesium carbonate, barium carbonate and quartz flour (1, 3) are good purifiers of distilled water and extracts of soils.

Water extracts of certain unproductive soils are improved by shaking them with carbon or ferric hydrate and filtering the solution clear (2, 3). Experiments were made to ascertain whether certain poor soils would be improved by the addition of carbon and other finely divided materials direct to the soil. These experiments were made first in pots in the greenhouse, using soils which had grown the same crop repeatedly for a number of times and had become very poor. The productivity of these soils was not restored by fertilizers. Carbon black was added to and mixed with the soil in an attempt to absorb anything of a harmful nature from the soil, but the soil was not thereby improved for plant growth. In a field experiment on the Arlington Experimental Farm carbon black was added on plots growing wheat, rye, timothy, clover, corn, cowpeas, and potatoes. This experiment was conducted for six years, the same crop having been grown on the same plot each year. The carbon had no beneficial effects on any of the plots. These experiments were made by mixing the carbon with the soil. Although the carbon might have had an absorptive action in taking up substances of a harmful nature, it was nevertheless in close contact with the soil and plant roots. On this account it might be expected that no beneficial action would be shown. Similar experiments were made, in which ferric hydrate and magnesium carbonate were used, but no uniformly beneficial results were secured.

Experiments were made in similar soils by putting the carbon in porous pots, tubes, and jars and burying them in the soil. The tubes used were very porous, permitting the moisture of the soil to pass freely through the

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[1] Received for publication June 30, 1916.

carbon and out again. Through the use of this method the absorbing material was not brought in contact with the soil itself or with the plant roots, but was able to absorb materials from the soil solution. If the soil contained soluble, harmful organic substances they would to a certain extent be absorbed and removed from the solution. Experiments bearing on this problem were made and are presented in the following pages. The carbon black used throughout this investigation is made by burning natural gas and collecting the carbon on cooled cylinders. It is known as the "G Elf" brand and was secured from G. L. Cabot and Co., Boston, Mass.

EFFECT OF CARBON BLACK INCASED IN POROUS MATERIAL ON GROWTH IN POTS

Several experiments were made in pots, carbon black being placed in a smaller pot of porous earthenware material and then buried in the soil in the larger pot in which the plants grew. The carbon black used in these experiments was thoroughly washed and packed in the small pot in a moist condition. The pots were the ordinary unglazed flower pots used in general greenhouse work. On account of the porous character of the pots water added to the soil during the experiment could circulate easily through the soil into the incased carbon and back again through the walls of the inner pot into the soil in which the plants were growing. The roots of the plants could in no way come in contact with the carbon black, as the top of the inner pot was covered in such a way that the soil could not mix with the carbon.

A soil was used for this first experiment which had grown cowpeas in the greenhouse, crop after crop for two years. The soil had become very poor and produced very poor cowpeas. The soil was potted in 8-inch earthenware pots and a 4-inch pot was filled with carbon and buried in the center of the 8-inch pot. In the other pot, which was to serve as a check, the small inner pot was filled with some of the same soil as the larger pot. Nine cowpea plants were planted around the circumference of the pots 1 inch from the walls. The seeds were planted March 10, 1910, and grew for 6 weeks. The growth in the two pots at an early period of the experiment is shown in Plate I, (fig. 1). Pot No. 1 is the check and No. 2 contains the carbon black. It is shown here that the growth at this early stage is better in the pot containing carbon. The green weight of the nine plants at the end of six weeks for the carbon pot was 17.8 gm. against 13.9 gm. for the check plot, an increase of 29 per cent.

A similar experiment was made growing wheat in a sandy loam soil. This soil when used in the greenhouse in pots and boxes grew good wheat. Pots of the same size as those described under the preceding experiment were used. Ten wheat plants grew in each pot and were planted around the circumference as in the case of the cowpeas. The wheat was planted

March 10 and the green weights taken April 11. The growth in the two pots was practically the same. The check pot produced 10.3 gm. green weight, while the green weight of the plants in the carbon pot was 10.4 gm.

Another experiment was made with wheat. This time a poor silty clay loam from the Arlington Experimental Farm was used. Eight-inch pots were used and the carbon, as before, was incased in a 4-inch pot and buried in the soil of the larger pot. Ten wheat plants were grown in each pot for 4 weeks. The green weight of the plants in the check pot was 3.9 gm. and that of the pots containing carbon was 6.6 gm., an increase of 70 per cent.

Still another test of this nature was made. The soil used was taken from the Smithsonian grounds and was so situated that it received the drainage and dripping from maple trees. Lawn grass in this section of the park invariably fails. Manure, lime, and commercial fertilizers have been used in attempts to secure a lawn, but with the same result, a complete failure. This ground was annually dug up and re-seeded in the early spring for several years, but the grass always failed.

The lawn soil was used in 8-inch pots as before. In one of these pots carbon incased in a small earthenware pot was buried, and in another, which was to serve as a check, the small buried pot was filled merely with the same soil used in the experiment. A mixed lawn grass seed was sown, the same amount in each pot. The grass was seeded April 12 and was cut for the first time May 11. A second cutting was made June 6, and a third June 28. The green weights of the grass are given in Table I.

TABLE I

EFFECT OF CARBON BLACK ON THE GROWTH OF GRASS IN A POOR LAWN SOIL

	First cutting gm.	Second cutting gm.	Third cutting gm.
Check	6.7	8.0	5.5
Carbon	10.6	10.0	9.0

The figures in the table show that the carbon had a very beneficial effect in this soil.

The same soil was used in a similar experiment in which clover was grown instead of grass. The check pot and carbon pot growing clover are shown in Plate I (fig. 2). The clover was planted April 12 and cut and weighed June 14. The green weight of the check pot was 90.0 gm. and that of the carbon pot 105.5 gm.

The beneficial action of carbon incased in porous material in these poor soils can be attributed only to its absorbing qualities. It would seem that the soil moisture, passing through the carbon, is robbed of its harmful material, whether organic or inorganic, gaseous or liquid, and the purified soil solution passing again into the soil becomes a better medium for the growth of plants.

EFFECTS OF CARBON BLACK IN POROUS BATTERY JARS IN SOIL IN GREENHOUSE BENCHES

The principle of the adsorption of harmful organic material by carbon black from poor soil was tried on a larger scale with soil on greenhouse benches. The bench used is 3 feet 6 inches wide and 8 inches deep. Partitions were placed in the bench 18 inches apart. This makes a frame 36 inches by 18 inches by 8 inches and holds approximately 250 pounds of soil. In this type of experiment, battery jars of very porous material were used. The jars are 6 inches long and 2¾ inches in diameter. They were filled and well packed with moist washed carbon, corked and buried in the soil. The jars were laid in the bed in two parallel rows, five to each row. Each row of jars was approximately 6 inches from the side of the frame and the rows were 6 inches apart. They were covered with approximately 4 inches of soil. One frame contained the jars filled with carbon. To serve as a check, the adjoining frame contained the same number of jars filled with some of the soil used in the beds.

The soil used in this experiment was taken from the flower gardens of Mount Vernon, Virginia. This soil has been under investigation by this office for several years. Some parts of the garden are producing unsatisfactory growth in spite of the fact that the soil has been well manured. Salicylic aldehyde and several other organic compounds were found in soil from certain sections of the Mount Vernon garden in former investigations and this particular sample taken for the present investigation, when subjected to the chemical process for isolating aldehydes, revealed a substance which gave the aldehyde reactions with certain chemicals, showing the presence of this class of substances in the soil (4, 5).

String beans were planted in the soil in the soil fertility greenhouse at Arlington, Va., November 1, 1915. Two rows of beans were planted in each bed, each row being over a row of tubes. The rows of beans were 6 inches apart, with 7 hills in each row. Two plants were grown in each hill, making 14 plants in each bed. The beans grew and produced fruit. They are shown in Plate II (fig. 1). The bed on the left is the check bed and contained the jars filled with soil; the bed on the right contains the jars filled with carbon. From the illustration it is seen that the carbon bed has produced the greater growth. The beans were picked and vines cut January 15, 1916, having ceased to produce fruit. The weight of the check bed was 250.0 gm. of vines and 162.5 gm. of beans in the pod and the weight of the carbon jar bed was 390.0 gm. of vines and 250.0 gm. of beans.

Other experiments of this kind were made by adding harmful organic compounds, namely, vanillin and salicylic aldehyde, to the soil in such amounts as to injure the growth. Porous jars filled with carbon were buried in the soil to determine whether or not the harmful materials would be absorbed from the soil, thereby improving the growth. Vanillin and salicylic aldehyde were selected as the organic compounds for this experiment as they have both been found to exist in some poor soils.

As in the former experiment, the bench beds were 36 inches by 18 inches by 8 inches. In one bed were placed 10 of the porous jars filled with carbon, arranged in two rows of 5 jars each, and in the adjoining bed the porous jars were filled with soil. The soil used in these beds was the silty clay loam, of moderate productivity, from the Arlington Experimental Farm. One of the vanillin treated beds contained porous jars filled with carbon and the other bed jars filled with the silty clay loam. Likewise, one of the salicylic aldehyde beds contained carbon tubes and the other soil tubes. A fifth bed having no treatment and no tubes buried in it was added as a check on the effectiveness of the aldehydes.

Fourteen bean plants grew in each bed. The seeds were planted November 1, 1915. Before planting, 5 gm. of vanillin and 3 gm. of salicylic aldehyde were added and mixed with the soil in their respective beds. Further quantities of vanillin and salicylic aldehyde were added to the surface in a water solution November 12, November 23, and December 3. The material was worked into the soil; each time 5 gm. of vanillin and 3 gm. of salicylic aldehyde were added, making a total of 20 gm. of vanillin and 12 gm. of salicylic aldehyde applied in the respective beds. This makes a total of 200 p.p.m. of vanillin for the two vanillin treated beds, and 120 p.p.m. of salicylic aldehyde for the two salicylic aldehyde treated beds. In Table II is given the yield of vines and pods from the different beds.

Considering the vanillin treated soil first, the growth in the bed which contained the carbon tubes was much better than the checkbed which contained the tubes filled with soil. Comparing the growth in both beds with that in No. 5, it is seen that the vanillin depressed the growth somewhat, but the harmful effect was overcome to a great extent by the absorption of the carbon. The growth in the two vanillin beds is shown in Plate II (fig. 2). The first bed contains the soil tubes and the second the carbon tubes.

The results with salicylic aldehyde were similar to those with vanillin. The growth in bed No. 4, which contained the carbon, was much better than that in the check bed No. 3. By comparing the growth in bed No. 5 with that in No. 3 and No. 4 it is seen that the salicylic aldehyde also produced a harmful effect. This too was partly overcome by the absorption of the carbon in the tubes. In Plate III (fig. 1) are shown the two salicylic aldehyde beds. The second bed contains the carbon tubes.

A similar experiment was made by growing lettuce in soil treated with salicylic aldehyde. In this experiment one bed contained tubes filled with soil and another bed tubes filled with carbon. The lettuce plants were transplanted November 1, 24 plants of Grand Rapids Curly Leaf variety having been placed in each bed. The amounts and time of application of aldehyde were the same as those given in the experiment with string beans. The lettuce grew rather poorly in this soil. The weight of that from the carbon bed was 645.0 gm. as compared with a weight of 600.0 gm. for the lettuce from the check bed, indicating a slightly better growth in the carbon bed.

TABLE II

EFFECT OF CARBON IN POROUS JARS, ON BEANS IN SOIL TREATED WITH VANILLIN AND SALICYLIC ALDEHYDE

Bed No.	Treatment	Porous jars buried in soil filled with	Green weight gm.	
			Vines	Pods
1	Vanalin	Soil	172.0	138.8
2	Vanillin	Carbon	225.0	194.0
3	Salicylic aldehyde..	Soil	185.0	139.5
4	Salicylic aldehyde..	Carbon	207.0	194.2
5	Untreated	(No jars)	241.0	209.8

A review of these experiments in greenhouse bench beds shows that in a garden soil in which harmful organic compounds of an aldehyde nature exist and in soil made unproductive by the addition of organic substances, such as vanillin and salicylic aldehyde, carbon incased in porous tubes buried in the soil improves its productivity, presumably by the absorption of the soluble organic substances from the soil solution by the carbon.

Effect of Absorbing Substances Incased in Porous Materials on Growth in the Field

Experiments were also made with carbon in tubes buried in plots in the field. The experiment was enlarged in this case. Several materials, all having absorbing qualities were used, namely carbon black, wood charcoal, chalk ($CaCO_3$) and magnesium carbonate. In addition to using the battery jars, specially constructed concrete tubes and very porous tile drain were used. The cement tubes were made by coating a wire gauze tube with cement, thus making a very thin layer, which is very porous and permits water to pass through freely. These tubes were 2½ inches in diameter and 3 feet long. They were filled with the absorbing material and the ends closed with corks. The other tubes consisted of unglazed earthenware tile drains, which were very porous and permitted water to pass through freely. These were 2¾ inches in diameter and 1 foot long. They were filled and corked at each end in the same manner as the concrete tubes. This porous tubing was buried in the plots before the ground was seeded. Trenches were dug and the tubes laid 8 inches beneath the surface and under the rows where the plants were to grow.

These experiments were made at the Arlington Experimental Farm and in soil which had been growing cowpeas for 6 successive years. These plots are unproductive and produce small yields. The soil is an acid one, having a lime requirement of approximately 2000 pounds of $CaCO_3$ per acre. It requires periodical liming to keep the soil neutral.

Carbon black. Cowpeas were grown in rows 16 feet long and 2 feet apart. Under 4 rows tubes filled with carbon were buried and adjoining them were grown 4 rows as a check, which had no tubes. Some of these tubes were of concrete, some consisted of porous tile drain, and some of battery jars. This experiment was started in the spring of 1914 and 2 years' results were secured. Cowpeas were planted in the spring and grew to maturity, when they were cut and the weight of the cured hay taken. In 1914 the weight of the four rows with carbon tubes was 9 pounds and the weight of the check rows without tubes was 8 pounds, a slight increase of growth in the carbon plot. In 1915 the carbon plot produced 18¼ pounds of cured cowpea hay and the check plot 16 pounds. Both years there was an increase in the carbon plot.

Charcoal. This test was similar to the one with carbon, just described, except that only 2 rows of tubes were used and 2 check rows that had no tubes. The porous tubes were filled with powdered wood charcoal, which was moistened and well packed. The tubes were buried in the soil in the spring of 1914, and cowpeas grown in 1914 and again in 1915. In 1914 the two rows of cowpeas in the charcoal plot produced 6 pounds of cured hay and the check plot produced 3.6 pounds, an increase of 66 per cent for the charcoal plot. In 1915 the charcoal plot produced 12 pounds of dry cowpea hay and the check plot 6.6 pounds, an increase of 80 per cent for the charcoal plot.

Chalk. In another plot chalk ($CaCO_3$) was used in the porous tubes in order to determine whether finely divided chemicals of this character would have a similar effect to those which have only an absorbing effect. Calcium carbonate is practically insoluble in water. In addition to its effect as an absorbent it could have an effect on the soil solution passing through it by neutralizing or precipitating any acids that may be present. Three rows of tubes filled with chalk were buried in the soil, as in the experiment with carbon and charcoal. Cowpeas were grown in the rows in which the tubes were buried and also in three adjoining rows that were to serve as a check. In 1914 the weight of cowpea hay for the chalk plot was 7.0 pounds, and that of the check plot was only 3¾ pounds. In 1915 the differences were not so large; the chalk plot produced 12 2/3 pounds dry weight, and the check plot 10½ pounds. The growth in the first year of the experiment is shown in Plate III (fig. 2). The three rows on the left have the chalk tubes; the three rows on the right are without tubes.

Magnesium carbonate. Experiments were made with magnesium carbonate, which is finely divided and, aside from its absorbing qualities, would also produce a chemical reaction with the acids of the soil solution similar to that with chalk. Three rows of tubes were used, cowpeas being grown as before, and the growth was compared with that on three other rows growing beside them.

In 1914 the growth in the magnesium carbonate plot was 14 pounds and in the check plot 14¼ pounds, and in 1915 the weights for the magnesium carbonate plot was 18.0 pounds and for the check plot 17¼ pounds. The magnesium carbonate seems to have had practically no effect, for in the first year there was a reduction of one-quarter of a pound, and in the second year there was an increase of three-quarters of a pound.

The magnesium carbonate and its check plot were, however, on a different part of the farm from the plots on which the other tests were made. The plots with carbon, charcoal, chalk and their checks adjoined each other and the soil conditions were more likely to be similar, whereas the conditions in the part of the field where the magnesium carbonate test was conducted were probably very different. This is indicated by the greater yield in the plot. The effectiveness of the magnesium carbonate in this respect is therefore not ascertained by this test.

The contents of the tubes were examined chemically for absorbed or precipitated material by E. C. Lathrop of this laboratory. The carbon black and charcoal contained a small amount of a liquid fatty acid but no aldehydes could be isolated. The calcium carbonate and magnesium carbonate contained a small amount of fatty acids and showed the presence of aldehydes. The amounts in all cases were too small for further study. The fact that aldehyde reactions were obtained from the carbonates and not from the carbon and charcoal would indicate either a destruction of the aldehydes, possibly by oxidation through absorbed oxygen, or else that the aldehydes, when once absorbed, are tenaciously held by these substances.

SUMMARY

It is pointed out that finely divided carbon is a good agent for physiologically purifying distilled water and certain poor soil extracts, and that by its absorptive qualities it improves the solution as a medium for plant growth.

The test made by mixing carbon black with poor soils failed to effect an improvement, as the carbon, even though it might have had an absorptive action, would itself be intermingled with the soil and be in contact with the plant roots.

With carbon incased in porous earthenware pots buried in soil, the growth of grass, clover and cowpeas was improved when growing in a poor unproductive soil in the greenhouse.

On benches in the greenhouse a soil which contained salicylic aldehyde and other organic compounds was improved for the growth of string beans by the absorptive action of carbon buried in porous tubes in the soil.

In an experiment with string beans and lettuce in greenhouse benches a soil made poor by the addition of salicylic aldehyde and vanillin was improved in productivity by the action of carbon incased in porous tubes.

In a two years' field experiment carbon, charcoal, and chalk, when put in porous tubes and buried in the plots, caused a good increase in growth of cowpeas.

The beneficial action of carbon and other absorbents may be attributed to its removing something from the soil solution which is harmful to plants. The soil moisture passing through the carbon in its process of moving downward and upward in the soil would be robbed of any such material. Soils which contain soluble organic substances harmful to plants would be improved for crop growth.

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PLATE I

Fig. 1.—Effect of carbon black in a poor soil on cowpeas. (No. 1 check, No. 2 carbon black buried in the soil in a porous cup).

Fig. 2.—Effect of carbon black in a poor grass soil or clover. (No. 1 check, No. 2 carbon black buried in the soil in a porous cup.)

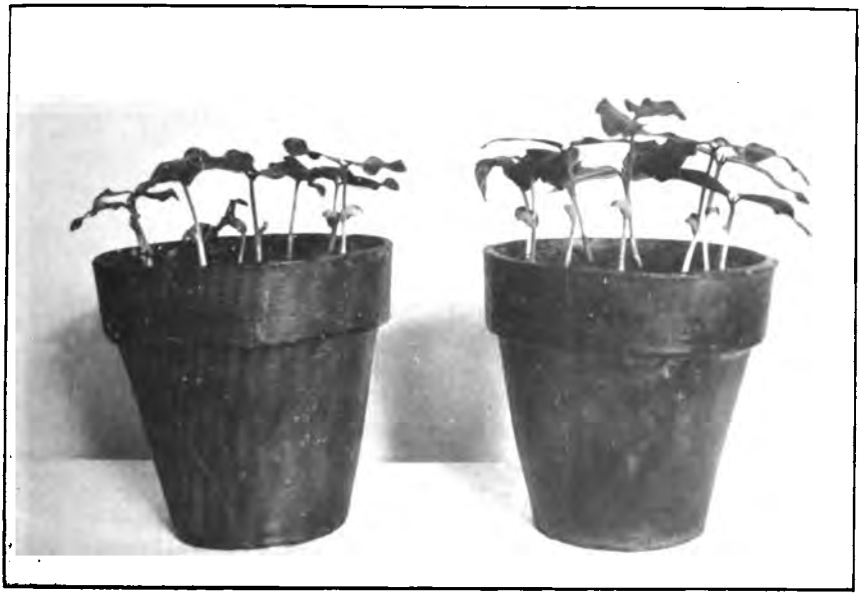

Figure 1

Figure 2

Figure 1

Figure 2

PLATE II

Fig. 1.—Effect of carbon in porous jars buried in a poor garden soil, on string beans grown on the greenhouse bench. (Bed on left contains jars filled with soil; bed on right contains jars filled with carbon black).

Fig. 2.—Effect of carbon black in porous jars in a soil to which vanillin was added, on string beans grown on the greenhouse bench. (Bed on right contains jars filled with soil; bed on left contains jars filled with carbon black).

PLATE III

Fig. 1.—Effect of carbon black in porous jars in a soil to which salicylic aldehyde was added, on string beans grown on a greenhouse bench. (Bed on left contains porous jars filled with soil; bed on right contains porous jars filled with carbon).

Fig. 2.—Effect of chalk in porous jars buried in the soil in the field, on cowpeas. (Jars filled with chalk under the three rows to the left; no chalk under the three rows on the right).

Figure 1

Figure 2

- *Presented at the International Wire & Cable Symposium, Atlantic City, November 18, 1999* -

THE IMPACT OF CARBON BLACK MORPHOLOGY AND DISPERSION ON THE WEATHERABILITY OF POLYETHYLENE

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ABSTRACT

Carbon black is one of the most widely used and most effective ultraviolet (UV) light stabilizers for plastics applications. Several important segments of the plastics industry rely on carbon black for UV stabilization of weather-resistant products, including telecommunications and power cable jacketing, plastic pipes, geosynthetic membranes and agricultural films. Recent research at Cabot Corporation confirms that the quality of the dispersion of the carbon black in a plastic medium (i.e. polyethylene) is an important component of both the UV-resistance and mechanical properties of the finished plastic article. There is a significant body of research into the linkage between carbon black morphology, including particle size, and UV performance. There is also anecdotal evidence demonstrating the linkage between dispersion quality and overall weatherability. In this study, Cabot will demonstrate that incremental improvements of carbon black dispersion can positively influence the expected life of plastic articles. With industry standard carbon blacks as a reference point, Cabot documents the morphological considerations of UV energy absorption and presents laboratory data demonstrating the link between dispersion and weatherability as well as between morphology and weatherability.

INTRODUCTION

Carbon black (CB) is more than a colorant. In addition to its tinting power, electrical or filler action, it provides plastics with a long-term and low cost UV protection, stabilising polyolefins and other polymers against sunlight [1-4]. The UV protection property of CB is dependent on its morphology, loading and surface chemistry. However if the CB is poorly dispersed or diluted, its full benefit will not be realized. These effects will be highlighted by comparative weathering results and UV absorption data obtained for low density polyethylene films.

1) Basic Information on Carbon Black

• Production

CB results from incomplete combustion or thermal cracking of a hydrocarbon raw material (**figure 1**). Nowadays almost all carbon black is manufactured by the *oil furnace process*: a highly aromatic feedstock is partially burned by atomization into a hot flame made of natural gas and preheated air, the reactor temperature reaching more than 1500°C. At the process end, *powder* (“fluffy”) or *pelletized* carbon black is collected. The oil furnace process permits efficient control of end product physical and chemical properties.

$$C_xH_y + O_2 \xrightarrow{\text{heat}} C + CH_4 + CO + H_2 + CO_2 + H_2O$$

Figure 1: partial oxidation of aromatic hydrocarbons.

• Form

Carbon black is a particulate form of industrial carbon which exhibits a *“quasi-graphitic”* microstructure (**figure 2**). The manufacturing process leaves various forms of oxygenated groups on carbon black layer planes: mainly phenolic, quinolic and carboxyl chemisorbed complexes [5]. During the nucleation process (**figure 3**), three to four layers form *crystallites,* which combine to form *primary particles* which continue to grow into *aggregates. Agglomerates* are a dense collection of aggregates formed due to the small distances between them and the strong van der Waals forces present. CB dispersion into a polymer matrix will require the breaking of these links. An *aggregate* is *indivisible* and represents the carbon black *“base unit”*, although a carbon black is often characterized by its *primary particle size*, as we will do further on.

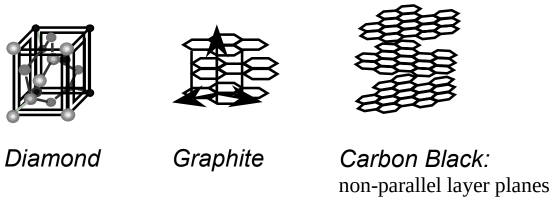

Figure 2: carbon black "quasi-graphitic" microstructure compared to the two regular crystalline forms of carbon (diamond and graphite).

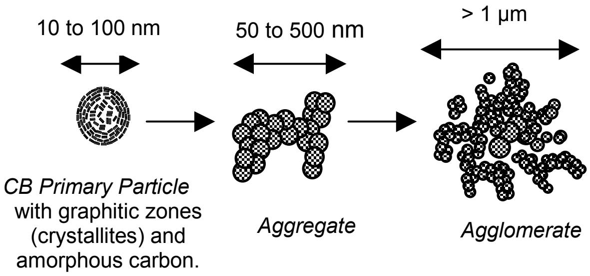

Figure 3: CB *primary particles* fuse together in the reactor and form *aggregates* and *agglomerates*.

2) Some Carbon Black Fundamental Characteristics (figure 4)

- **Particle size** (nm):

arithmetic mean of diameters of a sufficient number of primary particles of a carbon black grade. Diameters are determined by TEM (Transmission Electron Microscopy) measurements using ASTM D-3849.

- **Surface area** (m²/g):

specific surface area is determined by nitrogen adsorption capacity using the BET (Brunauer-Emmet-Teller) procedure. Small particles will confer a large surface area per unit weight.

- **Structure** or DBP oil absorption (ml/100 g):

the amount of DBP (di-butyl-phthalate) absorbed by 100g of carbon black at a fixed torque value, according to ASTM D-2414. Structure or the DBP adsorbed is function of the aggregates void volumes and describes the degree to which the CB particles have fused together to form aggregates: a low structure black (low DBP) is made of few primary particles compactly fused together while a high structure black (high DBP) is made of many primary particles with considerable branching and chaining.

3) Polyethylene Degradation

Finished materials designed for external applications may degrade in use, with time. They are said to *"weather"* when their structure changes due to *light, heat, moisture* and *oxygen* contact. Materials like plastics absorb sunlight radiations and undergo photo-chemical reactions. Oxidation occurs leading to an alteration of their colour, texture or composition resulting in impact loss, embrittlement, chalking or surface cracking. Out of the whole solar emission spectrum (range defined by CIE [6]), only the smallest part, the 290-400 nm UV region, is responsible for most of the polymer damage [7]. Photo-oxidation of polyethylene proceeds by a free radical chain mechanism in presence of oxygen: the ultraviolet light absorbed by the polyethylene provides sufficient energy to break key molecular bonds and generate free radicals that propagate to give *hydroperoxides*, compounds containing *hydroxyl, carbonyl and vinyl groups*, which also absorb UV radiation and undergo further degradative processes (i.e. Norrish type I and II reactions of the carbonyl group). As a result, succession of chain scissions and chain recombinations (cross-linking), including more fragile units, induces drastic physical degradations [1].

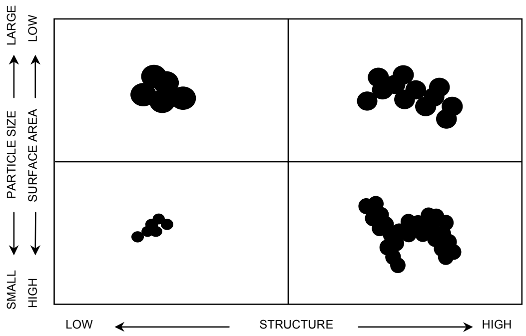

Figure 4: visualisation of carbon black *particle size / surface area* and *structure*.

EXPERIMENT

Polyethylene protection from UV degradation can be achieved by adding appropriate additives such as antioxidants, typical UV stabilisers (i.e. HALS) or carbon black. Parallel to its colorant function, carbon black is known to act as a UV absorber and antioxidant [8, 9]: it offers the best UV protection for many materials, by absorbing / screening out damaging wavelengths, and by inhibiting photo-oxidation via its surface chemical properties. The following experimental data highlight morphology, dispersion and dilution influence on carbon black UV stabiliser role.

1) Influence of carbon black morphology, emphasis on particle size [experiment 1]

Several black pigmented LLDPE (linear low density polyethylene) films were submitted to an accelerated weathering test.

Material lifetimes versus particle sizes and loadings are shown. CB morphology influence on weathering performance is discussed.

- **Sample preparation**

Cast films of 75 µm thickness were made from LLDPE Mi0.5 with 1.5, 2.5 and 3.5% CB of particle size ranging from 15 to 60 nm. Masterbatches were first produced at 35% loading on a 30 mm twin-screw extruder, then diluted to the above % in a second extrusion step. CB main characteristics are detailed in **Table 1**. The films were exposed in a QUV accelerated weathering machine at 60°C using UVA-340 nm (*) fluorescent lamps (ASTM G53-95) with no condensation cycle and irradiance level of 1.25 W/m²@340 nm. (*) Sunlight simulation in the region of 295 to 400 nm with max. at 340 nm.

- **Weathering results**

Tensile properties were measured on an Instron 4204 per ASTM D882-9. Failure time was determined when % elongation at break reached 50% of the original value. Material lifetime is expressed as a function of CB particle size, at the same CB loading (**figure 5**) and for various CB loadings (**figure 7**). Clear LLDPE film was also tested (**figure 6**).

Table 1. CB characteristics. **[Experiment 1]**

particle size ASTM D-3849 (nm)	*surface area* BET / N_2 ads. (m^2/g)	*structure* DBP abs. ASTM D-2414 (ml/100g)
63	30	72
50	41	125
24	78	72
23	79	102
18	120	114
15	252	68

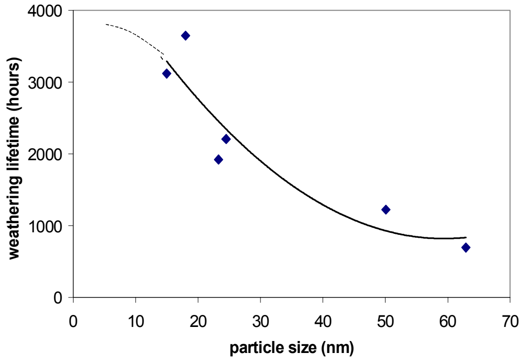

Figure 5. Influence of CB particle size - at same loading - on UV stability. (75 µm LLDPE films, 2.5% CB). **[Experiment 1]**

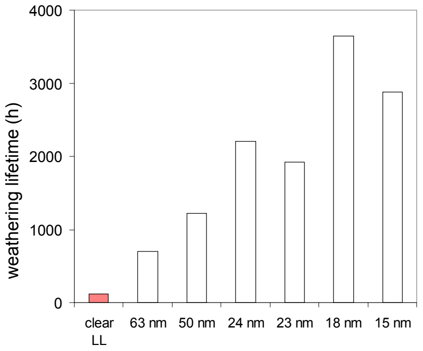

Figure 6. Weathering lifetime of clear LLDPE versus black LLDPE (75 µm, 2.5% CB). **[Experiment 1]**.

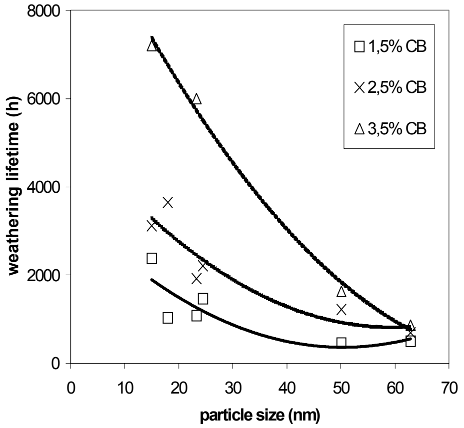

Figure 7. Influence of CB particle size - at different loadings - on UV stability. (75 µm LLDPE films, 1.5, 2.5% and 3.5% CB). **[Experiment 1]**.

- **Results discussion**

Virgin LLDPE exhibits very poor weathering stability. CB addition strongly improves weathering performance (**figures 5 and 6**): LLDPE lifetimes is 6 to 30 times higher when 2.5% CB is added. Maximum performance was achieved with CB with particle size <20 nm and high structure.

The UV stability effectiveness of a carbon black increases with decreasing particle size (as already reported in [10]) with some comments:

- close particle size blacks (e.g. 23 and 24 nm) may be differentiated by their structure. Lower structure tends to provide slightly better UV protection [11] provided the CB's are equally well dispersed.
- very small particle size blacks (e.g. 15 nm) see their protection benefit tempered by the difficulty to disperse them completely.

*The higher the CB loading, the better the UV protection. (**figure 7**)*

- CB loading may be limited by physical properties of the compound or other considerations.

In a paper to be published by J.R. Wilson [12], a theoretical model is proposed which shows the 2-dimensional projected surface area of the CB aggregate is directly correlated with its ability to absorb light. Hence, *both particle size and structure* (to a lesser extent) are important parameters affecting UV protection. However both of these parameters also affect dispersion characteristics, so in practice the actual performance of the carbon black in the compound is dependent on a number of factors.

2) Influence of Carbon Black Dispersion

Choosing small particle size blacks is a must to reach good weathering performances. However, to get that total benefit, care must be taken to disperse them correctly in the polymer matrix. Dispersion quality impacts the final carbon black agglomerate size in the polymer:

- an optimal dispersion is one that evenly distributes carbon black throughout a polymer down to the smallest carbon black units, the aggregates,
- a poorer dispersion results in larger agglomerates (**figure 3**).

In the presence of agglomerates, UV light is more likely to be rather scattered than absorbed, and polymer UV degradation may start as CB screening protective effect is reduced. *Accelerated weathering tests* **[experiments 2** and **3]**, transmitted *light measurements* **[experiment 2]** and *COA* (375 nm UV absorption coefficient) **[experiment 4]** have been carried out on well and deliberately badly (or less well) dispersed carbon blacks in low density polyethylene films. All other parameters were kept constant.

a) Effect of dispersion on weathering
[Experiment 2]

- **Film preparation**

- Three different CB, of various particle sizes, were analysed: 60, 25 and 20 nm.
- 30 to 40% CB masterbatches were prepared on a Banbury BR 1.5 mixer: the different CB were incorporated into LDPE Mi7 with a slight and constant amount of lubricant (0.1% lubricant per 10% CB).
- 2.5% CB compounds were obtained by diluting the above masterbatches in LDPE Mi4 and extrusion in a Betol BK32 machine (L/D=30; single screw extruder with additional CTM mixing unit).
- 55 µm cast films were made on a semi-industrial Collin extruder (L/D=27; compression ratio 3:1; 210°C).

The deliberately under-dispersed (UD) samples were obtained by reducing the Banbury mixing time and shear. **Table 2** summarises CB dispersion quality and films involved.

- **Dispersion quality assessment**

Via *Screen 100 mesh* (#) and *film* tests:

- The *screen 100 mesh* test consists of extruding 40 g of MB, slightly diluted in LDPE Mi2, through a Betol extruder ended with a 100 mesh screen. The number of particles trapped in the screen is then counted. Results are in “particle number”.
- The *film* test consists of making a 50 µm blown LDPE Mi0.3 film containing 1% of CB. The film is then sufficiently translucent for analysis by transmission on a light cabinet. Spots are detected by touch and visually counted. Results are in “speks per gram”.

- **Accelerated weathering test**

- Films were placed in an *ATLAS xenon arc machine* and exposed to the standard accelerated weathering norm for films ISO 4892-2, with conditions: ATLAS Ci65A machine, 6500 W xenon lamp, borosilicate-s / borosilicate-s filters (*), irradiance = 0.35 W/m²@340 nm, cycles = 102 minutes light followed by 18 minutes light + specimen spray, light cycle temperature = 65°C (BST), light cycle relative humidity = 65%. (*) Simulation of total solar emission spectrum, starting from 290 nm.
- Five rectangular 10 mm wide strips were submitted after exposure to a traction test using an Instron 4466 machine complying with ISO 527-3 norm. The percentage of elongation at break (% E at B) in function of weathering exposure time was recorded to trace material degradation.

- **Results and discussion**

- *Impact of dispersion on initial properties.*

Initial physical properties of a material are dependent on the sample preparation or sample “history” (resin type, loading, processing conditions, thickness…). Care was taken to work comparatively, to only link CB type and dispersion degree to weathering performance, all other parameters were similar.

Unaged materials’ initial elongation at break (**figures 8** & **9**) appears to be directly dependent on dispersion quality or “global dispersion ranking” (**table 2**): the better the CB dispersion quality, the better the initial physical properties; the poorer the dispersion or the higher the UD gap within same CB particle size, the higher that physical property difference (**table 2**, **figure 10**).

Table 2. Dispersion results and ranking (UD= under-dispersed). Description of films involved in **experiment 2**.

CB Type	Screen Test 100#	Film Test	**Global Dispersion Ranking**	Dispersion Comparison by CB Type		**Films Submitted To Weathering** **- *identification* -**
particle size	*particle number*	*speks per gram*	*from best (1) to worst (6) - arbitrary scale -*	*UD gap compared to reference*	*UD degree*	**LDPE 55µm 2.5% CB**
60nm	4	0.7	**1**	Reference = R		**60nm**
60nm ″UD″	9	0.8	**3**	(3-1) → = R **+2**	**″UD″**	**60nm ″UD″**
25nm	6	7.2	**4**	Reference = R’		**25nm**
25nm ″UD″	10	11	**5**	(5-4) → = R’ **+1**	**Little ″UD″**	**25nm little ″UD″**
20nm	5	0.5	**2**	Reference = R″		**20nm**
20nm ″UD″	10	>20	**6**	(6-2) → = R″ **+4**	**Very ″UD″**	**20nm very ″UD″**

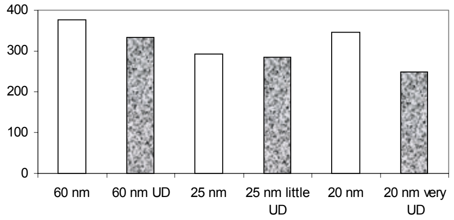

Figure 8. Initial % E at B of 55 µm LDPE films (2.5% CB). **[Experiment 2]**.

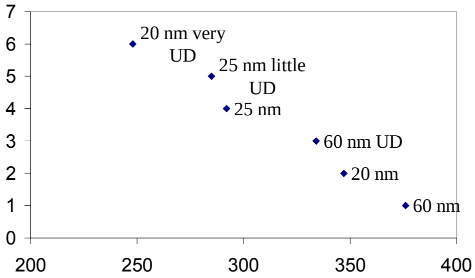

Figure 9. Dispersion quality ranking (1 = best dispersion, 6 = worst dispersion) in function of initial % E at B of films. **[Experiment 2]**.

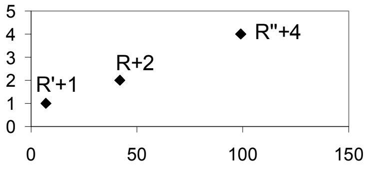

Figure 10. UD gap (within same CB particle size) in function of initial % E at B difference. **[Experiment 2]**

- Impact of dispersion on properties retention.

(**figure 11**) To make things objectively comparable, the initial *mean* % elongation at break has been indicated and a bold dotted line has been drawn at half that value: the test end limit is set at 175% E at B (in accordance with CEN for agricultural films recommendation + safety margin). Weathering lifetimes: see **figure 13**. Magnification of weathered films: see **figure 12.** UD gap versus lifetime loss: see **figure 14.** *Shorter weathering lifetimes are obtained with under-dispersed samples except for “25 nm” where UD gap is the smallest. The highest UD gap induces the highest lifetime difference.*

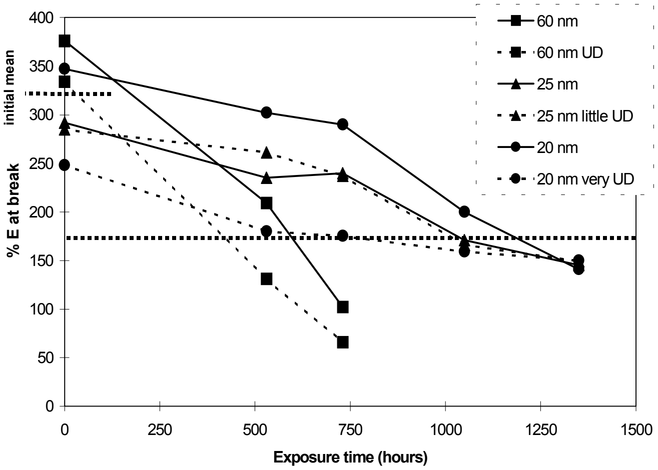

Figure 11. Dispersion influence on weathering stability - 55 µm LDPE films, 2.5% CB: Atlas xenon arc (ISO 4892-2 / ISO 527-3), % E at B in function of exposure time. **[Experiment 2]**.

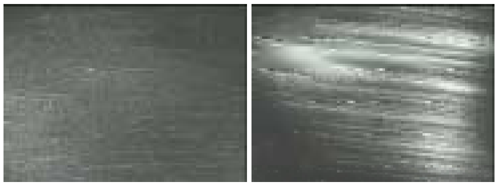

Figure 12. Magnification (15x) of weathered films - 800 hours ageing: *left*= 60 nm: *right*= 60 nm UD. **[Experiment 2]**.

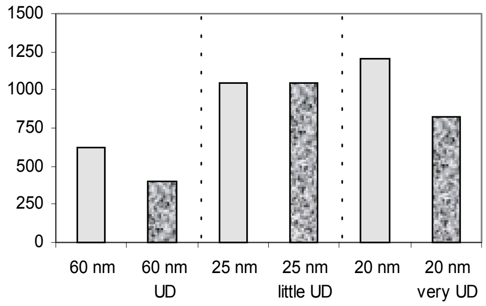

Figure 13. Film weathering lifetimes (hours) **[Experiment 2]**.

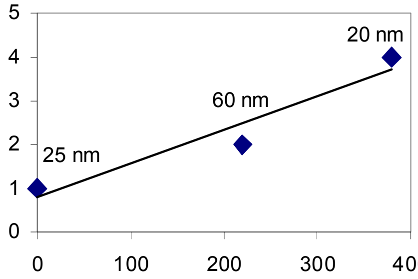

Figure 14. UD gap in function of lifetime loss (hours). **[Experiment 2]**.

- *Transmitted light study*

Films have been placed between a powerful 100,000 lux light source and a luxmeter with detection in the visible range. The number of lux transmitted through the film is expressed in **figures 15a, b**. Light transmission effectiveness is correlated to weathering performances (**figures 16a, b**). These figures, as well as **figure 11**, spot the 2 different groups: the 60 nm and the 25, 20 nm. First group transmits more light, second group is more effective to trap it. Additionally, *the UD films transmit more light or absorb less, inducing worse UV stability, except the "25 nm" where UD gap is very low.* Initial visible light transmission data are linked with UV stability data.

- **Results Discussion**

Weathering and opacity results are in line: the lower the transmission (higher the opacity), the better the UV stability. Both are function of CB type and %, film thickness, and on a microscopic scale, seem a function of dispersion. Poor dispersion induces lower opacity and poorer weathering performances. From what we may deduce dispersion and UV stability are directly dependent, with however a major impact of dispersion on initial physical properties.

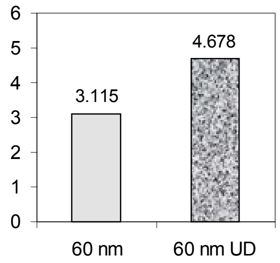

Figure 15a. Transmitted light (Lux). **[Experiment 2]**.

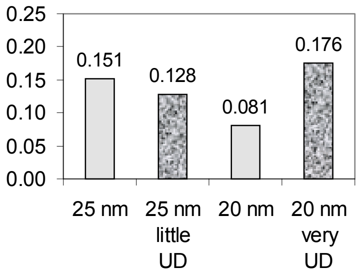

Figure 15b. Transmitted light (Lux). **[Experiment 2]**.

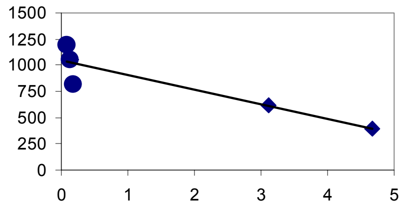

Figure 16a. Lifetime (hours) in function of transmitted light (Lux). **[Experiment 2]**.

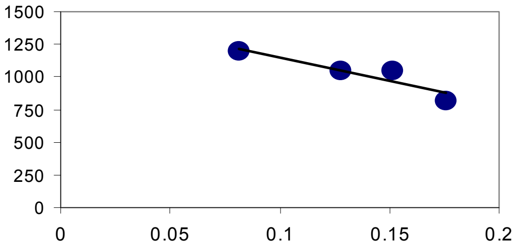

Figure 16b. Lifetime (hours) in function of transmitted light (Lux). (= Zoom of a **16a** region). **[Experiment 2]**.

b) Effect of dispersion on weathering
[Experiment 3]

• Weathering results and discussion

Table 3. **Experiment 3** results. * *bad dispersion*

CB Particle size *nm*	Failure Time *days to reach 50% retention*
None	5
60	21
19	43
15	*99*
15	*39**

Above film samples (1.5% CB) were prepared and tested as in **experiment 1**. The 15 nm CB sample which exhibited shorter than expected failure time was examined for dispersion quality. Thin sections (100 nm) were prepared using an RTE ultra-cryomicrotome then viewed at 50,000X magnification by Transmission Electron Microscope. Numerous agglomerates of CB were detected, as illustrated in **Figure 17**. The other film samples, examined in a similar manner, showed no such defects. *These results also clearly show the impact of bad dispersion on weathering performance of the LLDPE.*

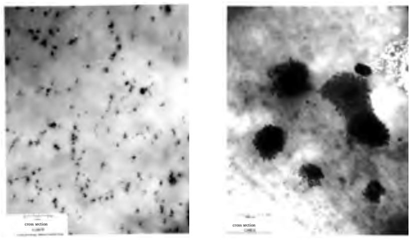

Figure 17. TEM images: *left*= 15 nm CB sample "good dispersion"; *right*= 15 nm CB sample "bad dispersion".

c) Effect of dispersion on COA
[Experiment 4]

• Sample preparation

Three CB with different primary particle sizes were compounded into LLDPE Mi20 resin on a laboratory size Kobelco internal batch mixer at three different loadings (**table 4**). Masterbatches (except 2.5%) were then letdown (i.e. diluted) in LLDPE Mi0.7 using the Kobelco mixer to 2.5% CB loading.

Table 4. Experiment 4 samples

CB particle size *nm*	CB masterbatch loading *%*
19	35, 20, 2.5
25	40, 20, 2.5
60	50, 20, 2.5

• Coefficient Of Absorption

COA was measured per ASTM D-3349*. This test measures the amount of light transmitted through a black pigmented film (typically less than 5% CB). Conversely, the amount of light *not* transmitted is absorbed, forming the basis for the calculation of the COA parameter (Beer's Law).

COA test procedure*:

1. Thin films are pressed to approximately 0.01mm.
2. Samples are exposed to UV light at 375 nm wavelength using a Beckman Model B spectrophotometer.
3. COA is calculated based on the absorbance value and sample thickness.
4. COA units are (1000 absorbance unit / meter).
5. ASTM D-3349 Least Significant Difference (within lab): Sr = 24.

• Dispersion evaluation

Dispersion was evaluated using image analysis. Six small pieces of each sample were pressed on a glass slide at 215°C for 5 minutes. The pressings were examined at 100X magnification. Agglomerates were sized and counted using Kontron Image Analysis software. Results are shown in **figures 18** and **19**.

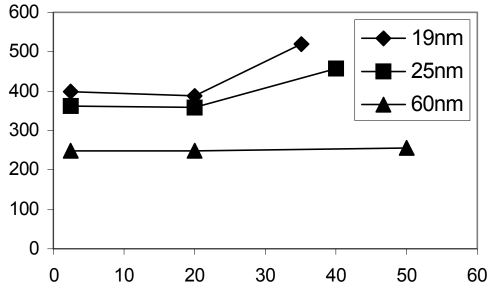

Figure 18. COA versus initial masterbatch loading (% CB) - for different CB particle sizes, at 2.5% CB in final letdowns. **[Experiment 4]**

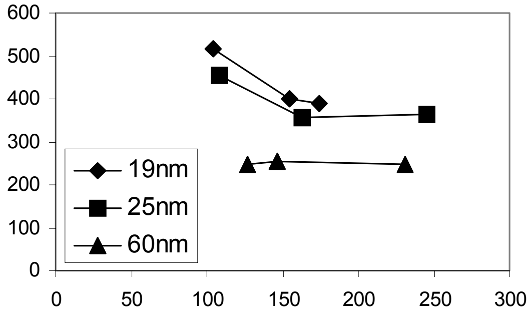

Figure 19. COA versus total agglomerates (# of pips), for different CB particle sizes at 2.5%. **[Experiment 4]**

Results discussion

COA shows a significant improvement at higher masterbatch loadings for the 19 nm and 25 nm CBs, presumably from better dispersion resulting from increased shear stress at higher masterbatch viscosity. The COA for the more easily dispersable 60 nm CB was flat over the range of loading studied. For the 19 nm and 25 nm CB the COA was highest for samples which had the fewest total agglomerates, an indicator of dispersion quality.

3) Influence of Carbon Black Dilution

• Experimental results

In **experiment 2** dispersion study, films were made via the masterbatch *and* compound route: the cast film extrusion line used did not mix and homogenize material sufficiently well to work directly with masterbatches. Without that last compounding step, films would have been very poorly diluted and full of fragile, less concentrated zones. We included however in the same study an additional film (19 nm CB) based on direct dilution. **Figure 20** shows comparative weathering evolution for “good” and “poor” dilution quality.

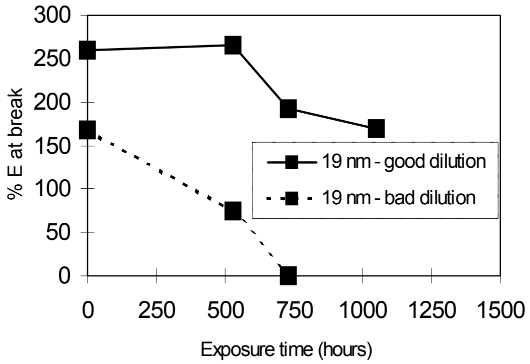

Figure 20. dilution influence on weathering stability - 55 µm LDPE films, 2.5% CB: Atlas xenon arc (ISO 4892-2 / ISO 527-3); % E at B in function of exposure time. [**Experiment 2+**].

• Discussion

A bad dilution can adversely affect polymer performance and weathering stability. The way to incorporate CB in a polymer matrix must be in total harmony with the equipment design and requirements or vice versa.

CONCLUSION

Black polymer UV resistance prediction is always a combination of several parameters, especially CB morphology, loading and dispersion quality. This study has demonstrated the very positive influence of small particle size CBs on polyethylene weatherability as well as the importance of good dispersion and dilution quality to maintain that benefit. Although dispersion quality is mainly affecting the initial physical properties of the films, retention of those properties with ageing time has been shown: physical property drop appears to be directly dependent on the dispersion degree. These results were consolidated with light transmission data which show an increased transmission with poorly dispersed samples.

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Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence

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Abstract

The aim of this work was to investigate changes in molecular form and surface charge of black carbon (BC) due to long-term natural oxidation and to examine how climatic and soil factors affect BC oxidation. Black C was collected from 11 historical charcoal blast furnace sites with a geographic distribution from Quebec, Canada, to Georgia, USA, and compared to BC that was newly produced (new BC) using rebuilt historical kilns. The results showed that the historical BC samples were substantially oxidized after 130 years in soils as compared to new BC or BC incubated for one year. The major alterations by natural oxidation of BC included: (1) changes in elemental composition with increases in oxygen (O) from 7.2% in new BC to 24.8% in historical BC and decreases in C from 90.8% to 70.5%; (2) formation of oxygen-containing functional groups, particularly carboxylic and phenolic functional groups, and (3) disappearance of surface positive charge and evolution of surface negative charge after 12 months of incubation. Although time of exposure significantly increased natural oxidation of BC, a significant positive relationship between mean annual temperature (MAT) and BC oxidation (O/C ratio with $r = 0.83$; $P < 0.01$) explained that BC oxidation was increased by 87 mmole kg C^{-1} per unit Celsius increase in MAT. This long-term oxidation was more pronounced on BC surfaces than for entire particles, and responded 7-fold stronger to increases in MAT. Our results also indicated that oxidation of BC was more important than adsorption of non-BC. Thus, natural oxidation of BC may play an important role in the effects of BC on soil biogeochemistry.

1. INTRODUCTION

Black carbon (BC) is the residue of incomplete combustion of biomass or fossil fuel. Black C is regarded as a chemically and biologically very stable C pool and can persist in nature for long periods of time (Goldberg, 1985; Schmidt and Noack, 2000; Knicker, 2007). Charring biomass into BC therefore has been proposed as a way to divert C from a rapid biological C cycle into a slow geological C cycle (Kuhlbusch and Crutzen, 1995) and prompts investigations into actively managing BC as a means to sequester atmospheric carbon dioxide in soils (Lehmann et al., 2006; Lehmann, 2007a,b).

However, the long-term persistence of BC does not mean that the properties of BC remain unchanged after its deposition. Puri (1961) and Cheng et al. (2006) have reported rapid oxidation of BC in short-term incubations, whereby BC properties were altered through the formation of oxygen-containing functional groups. Oxidation of BC in soils has important implications for BC transport (Hockaday et al., 2006), erosion (Rumpel et al., 2006), stability (Bird et al., 1999; Czimczik and Masiello, 2007), and cation retention (Liang et al., 2006). Up to now, however, systematic research about the natural oxidation of BC in soils remains scarce and little is known about such aspects as to how fast or to what extent BC is oxidized.

In addition, because BC is ubiquitous and found in a wide variety of environments (Goldberg, 1985), it is essen-

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tial to investigate the differences of natural oxidation of BC under different climatic and soil regimes. We know that oxidation and decomposition of organic matter and litter typically increase with temperature (Davidson and Janssens, 2006). However, our understanding of the factors that affect natural oxidation of BC across different climates is limited. Biotic (Hamer et al., 2004) and abiotic processes, such as greater temperature (Puri, 1961; Cheng et al., 2006) and moisture (Billinge and Evans, 1984), may facilitate BC oxidation, while aggregate protection of BC (Glaser et al., 2000; Brodowski et al., 2005) promoted in fine-textured soils may reduce BC oxidation. To what extent these processes affect oxidation of BC in soils across a range of different environments is not known.

Due to the high recalcitrance of BC, designing suitable laboratory or field experiments to investigate the long-term natural oxidation of BC is a challenge. In this study, we made use of BC samples from historical charcoal blast furnace sites in Quebec, Canada and the eastern U.S. These historical BC samples had similar deposition time, charring conditions and precursor wood. In addition, new BC made by the same method as the historical BC was collected to represent the "original" BC and was compared to the historical BC samples retrieved from soil. The wide geographic distribution of charcoal blast furnaces also made it possible to examine climatic and soil effects on historical BC samples. Our objective was to investigate changes in molecular form and surface charge of BC due to long-term natural oxidation along a climosequence. We hypothesized that long-term natural oxidation of BC leads to significant changes in both molecular form and surface charge and that the extent of BC oxidation is facilitated by greater temperature, moisture and biological activity but reduced by higher soil clay contents.

2. MATERIALS AND METHODS

2.1. Historical and new BC samples

Historical BC samples were collected from the remnants of historical charcoal blast furnaces. The BC found in soils near these furnace sites was only deposited during a relatively short period around the 1870s, as the rapid depletion of forest resources soon led to the replacement of charcoal furnaces by anthracite furnaces (Warren, 1973). The charcoal used for the blast furnaces was only produced from specific hardwoods. High specific gravity, crushing strength, and density were required, which was found in woods such as chestnut, hickory, oak, and sugar maple (Bining, 1938). In contrast to BC produced in forest fires, historical BC generated by colliers (charcoal workers) was of relatively uniform quality (Rolando, 1992).

In the 19th century, every eastern state in the U.S. (except for Delaware) had at least one furnace. In this study, eleven historical charcoal furnaces sites, spanning along a climosequence from Quebec (QC) to Georgia (GA), were selected. Some historical background and the climatic and soil characteristics of the selected furnace sites are shown in Table 1. Mean annual temperature (MAT), mean annual precipitation (MAP) and potential evapotranspiration

Table 1
Historical backgrounds and the climatic and soil characteristics of the selected historical charcoal blast furnaces in Canada and the U.S.

Location		Vegetation type[b]	Abandoned year	MAT[c] (°C)	MAP[d] (mm)	PET[e] (mm)	Soil properties						
							C (g kg^{-1})	N (g kg^{-1})	pH (H_2O)	pH (KCl)	Silt (g kg^{-1})	Clay (g kg^{-1})	C_{min}[f] (g kg soil^{-1})
QC[a]	Trois-Riviera	G	1883	3.9	1030	470	404	6	4.9	3.7	260	230	1.07
NY	Port Henry	BL	1875	6.2	900	610	300	7	6.2	4.9	220	190	1.61
CT	Canaan	BL/G	1918	9.4	1190	635	364	4	7.2	6.4	170	220	0.71
PA-1	Huntingdon	BL	1874	9.4	940	635	303	6	7.2	6.6	210	280	1.46
PA-2	Huntingdon	C	1904	9.4	940	635	520	5	4.8	3.7	230	240	0.70
NJ	Oxford	BL	1884	10.0	1150	660	176	3	5.9	4.7	240	260	0.63
OH	Jackson	G/BL	1894	11.1	1070	755	212	2	6.1	5.0	180	340	0.23
MD	Snow Hill	C	1894	13.3	1030	710	165	2	4.5	2.8	210	80	0.47
KY	Cadiz	BL	1860	13.6	1290	850	250	4	6.5	5.4	170	500	0.87
TN	Dickson	BL	1850	14.4	1370	845	224	3	6.1	4.1	270	540	1.11
GA	Cartersville	BL	1864	15.7	1210	865	130	3	5.8	4.8	270	310	1.13

[a] Abbreviations of the province of Canada and the states of the U.S.
[b] Vegetation type: G, Grass; BL, broadleaf; C, conifer.
[c] MAT: mean annual temperature.
[d] MAP: mean annual precipitation.
[e] PET: potential evaportranspiration.
[f] C_{min}: potential cumulative mineralized C (g C—CO_2 per kg soil) for a 20-day incubation at 30 °C.

(PET) for each site were obtained from long-term climate data of the closest recording station. Effective precipitation was defined as MAP minus PET (MAP – PET) and was used to represent soil moisture conditions (Clark and Royall, 1995). Samples of soils containing high levels of BC (BC-containing soils) were collected from the areas where furnace workers temporarily stored the charcoal before charging it into the furnace. Dark black soil color and even large BC fragments are conspicuous in these BC-containing soils. For each soil, at least five soil cores were collected.

Since we focused on the natural oxidation of BC itself and intended to minimize any artifact caused by adhering soil or organic matter, more than 40 large fragments of BC with a size over 4 mm, which were carefully picked from soil samples at a depth between 0.1 and 0.2 m, were pooled and used in this research. Isolated BC fragments were repeatedly rinsed with distilled water until the electric conductivity was close to the background of distilled water. The BC fragments were then oven-dried at 70 °C for 24 h for further analyses.

In addition to the historical BC samples, new BC samples produced in Pennsylvania at the Hopewell Furnace National Historic Site (New-BC$_{HW}$) and at the Greenwood Furnace State Park (New-BC$_{GW}$) were collected. Both of these new BC samples were made by the same traditional charcoal-making method, as done by charcoal workers in the 19th century. Charring conditions were carefully tended by the park rangers to obtain a high-quality metallurgical charcoal (Rolando, 1992). A mixture of white and red oak was charred at Hopewell (NEW-BC$_{HW}$), and only white oak wood was charred at Greenwood (NEW-BC$_{GW}$). The new BC samples are expected to have properties that were very close to the “original” status of the historical BC samples and were taken here to represent time-zero BC samples. The collected new BC samples were stored in glass jars purged with nitrogen gas to prevent further oxidation.

In order to provide the fundamental understanding of long-term natural oxidation of BC, new BC from the Hopewell Furnace (New-BC$_{HW}$) was subjected to short-term aging experiments and coating with humic acid (HA; Sigma–Aldrich, St. Louis, Missouri, USA) for simulating short-term BC exposure in soils. In the aging experiments, 4 mL deionized water was added to 10 g of new BC and incubated in the dark inside 500-mL glass jars at 30 °C and 70 °C for 12 months (denoted as BC30 and BC70) or at 70 °C for 6 months (denoted as BC70$_{6M}$, only for XPS analysis). Glass jars were opened for aeration, as well as verification and adjustment of the water contents, every week for the first two months and then every other week during the rest of the incubation. It was expected that a higher temperature would enhance the degree of oxidation compared to a lower temperature (Cheng et al., 2006). No inoculant was added, as the oxidation during the first few months was expected to be dominated by abiotic processes (Cheng et al., 2006). In the experiment of coating BC with HA, HA solution was prepared by dissolving 200 mg HA in 50 mL 0.1 N NaOH solution, and deionized water was added to make up the 200 mg L^{-1} HA solution. Forty milliliters of 200 mg L^{-1} HA solution were added to 2 g of BC and shaken for 3 days. Throughout shaking, the pH of the BC slurry was adjusted by 1 N HCl to a constant pH value of 6.8. After coating, the BC was washed with deionized water until the color of the filtrate was clear and reached a constant pH and then oven-dried at 70 °C for 24 h. The dissolved C of filtrates for both BC slurry and control HA solution was measured by a carbon analyzer (Model 1010 TOC Analyzer, OI Analytical, Texas) and the difference of dissolved C concentration was assumed to be the adsorption of HA. In this study, 2.52 mg HA were sorbed to 1 g of BC.

2.2. Analyses of BC fragments and soils

Total C and nitrogen (N) concentrations of BC fragments were measured by dry combustion using a Europa ANCA GSL sample combustion unit (PDZ Europa, Crewe, UK). Hydrogen (H) concentrations were measured after BC sample conversion to H_2 at 1400 °C over glassy C (Hekatech TCEA, Hekatech GmbH, Wegberg, Germany). Ash content was analyzed by the loss of weight via combusting the BC sample at 550 °C for 2 h. Oxygen (O) concentrations were determined by difference. Elemental composition of C, N, H, and O of BC samples were presented on a dry ash-free basis.

In addition to the BC fragments, the properties of BC-containing soils were measured as well. Total C and N concentrations of the BC-containing soils were measured by dry combustion. Soil texture was measured on adjacent soils which contained no visible BC particles using the hydrometer method. Potential soil biological activity was evaluated by measuring the cumulative soil C mineralization rate of the BC-containing soils over a 20-day incubation period. The incubation was carried out at the same temperature of 30 °C for all soils in the dark under 60% water holding capacity. The evolved CO_2 was trapped in 10 mL 0.1 N NaOH, which is placed in a small vessel inside the incubation jar, and measured by titration of the NaOH solution with standard 0.1 N HCl in excess of $BaCl_2$. The mineralized CO_2 was displayed per unit soil (g C—CO_2 kg soil^{-1}). Soil pH was measured in 1:2.5 (w/v) ratio with H_2O or 1 N KCl solution. In this study, pH values in BC fragments (1:20 w/v ratio) were close to the corresponding pH values in BC-containing soils.

2.3. X-ray photoelectron spectroscopy (XPS)

XPS measurements were conducted at the Wiley Environmental Molecular Sciences Laboratory using a Physical Electronics Quantum 2000 scanning ESCA Microprobe (Physical Electronics GmbH, Ismaning, Germany). The 98-W, 107-μm diameter X-rays were rastered over a 1.4 by 0.2 mm rectangle on the sample. The XPS survey scan spectra in the 1000–0 eV binding energy range were recorded with a pass energy of 50 eV. High-energy resolution scan spectra of C1s were recorded in 0.2 eV steps with a pass energy of 20 eV. Low energy electrons and Ar ions were conducted for specimen neutralization in each measurement. In this study, XPS measurements were performed on both intact BC particles and ground BC samples representing the surface and entire particle, respectively (Cheng et al., 2006). Here, unwashed intact BC particles of 1–2 mm in size were used. The approximate amount of O bound to C (Oc) was obtained by subtraction of the contribution of inorganic O from total O contents, and was calculated using the following equation (Brodowski et al., 2005):

$$\mathrm{Oc} = \mathrm{O}\ (\text{total O}) - (\mathrm{Na} * 0.5 + \mathrm{Mg} * 1 + \mathrm{Al} * 1.5 + \mathrm{Si} * 2 + \mathrm{K} * 0.5 + \mathrm{Ca} * 1 + \mathrm{Fe} * 1.176) \quad (1)$$

For the narrow scan C1s spectra, the spectra were deconvoluted by a non-linear least squares curve fitting program (XPSPEAK Version 4.1 software) with a Gaussian-Lorentzian mix function and Shirley background subtraction. The C1s binding energy for C═C, C—C and C—H was assigned to 284.6 eV. The shifts of the C1s binding energy were defined for 1.6 eV as C—O, for 3.0 eV as C═O, and for 4.5 eV as COO (Proctor and Sherwood, 1982). In this experiment, new BC and seven historical BC samples, including QC, NY, CT, OH, MD, TN, and GA, were measured.

2.4. Fourier transform infrared (FTIR)

The spectra of FTIR absorbance were recorded between 400 and 4000 cm^{-1} with a Matteson Model 5020 FTIR Spectrometer (Madison, Wisconsin, USA). Potassium bromide (KBr) pellets containing 0.3% of finely ground BC powder were prepared and scanned. One hundred scans from 400 to 4000 cm^{-1} were averaged with a resolution of 4 cm^{-1}.

In addition to the FTIR measurement of all BC samples, a series of pH adjustments of the QC and CT BC samples were also measured by FTIR. Basic and acidic QC and CT BC samples were obtained by adding 0.1 N HCl and KOH to the BC suspension (1:200 w/v ratio). The pH of the BC suspension was determined after shaking the suspension for 24 h and was applied to represent the adjusted pH of BC. Black C samples with pH adjustments were separated by centrifugation and dried at 70 °C for 24 h.

2.5. Surface charge characteristics

The surface charge of BC samples was assessed by the "index" or "indifferent" ion adsorption method (Uehara and Gillman, 1981; Chorover et al., 2006). A KCl electrolyte (0.01 N) was used in the present study, in which both K and Cl ions were assumed to be bound by non-specific adsorption. Briefly, the method comprised three main steps: (1) preparation of a KCl saturated BC paste, (2) adjustment of the pH of BC to a range of pH values under the same ionic strength, (3) displacement of adsorbed K and Cl by 1 N ammonium nitrate.

1. BC saturation by KCl: Two grams BC were suspended in 20 mL of 1 N KCl in 30 mL centrifuge tubes for end-over-end shaking for 1 h. The suspension was then centrifuged at 48,000 RCF for 20 min. The supernatant was carefully aspirated and discarded. The remaining BC paste was repeatedly suspended in 0.2 N KCl and 0.01 N KCl for one and two times, respectively. After the last centrifugation step, the remaining BC paste was transferred to a petri dish, sealed with paraffin, and stored at 4 °C. The water content of the BC paste was measured by transferring a small portion of the BC paste to an aluminum dish and drying it at 105 °C for 24 h.
2. pH adjustment: Around 0.15 g of the BC paste (on a dry weight basis) was transferred to 30 mL preweighed centrifuge tubes. Twenty milliliters 0.01 N KCl, adjusted by 0.1 N KOH or HCl across an adequate pH range under the same ionic strength, was added to a batch of the tubes. The tubes were shaken for 12 h and then centrifuged at 48,000 RCF for 20 min. The supernatant was carefully aspirated to a 30 mL bottle and the pH value was measured immediately. The concentrations of K and Cl in the supernatant were measured as well. The tubes with BC and entrained solution (0.01 N KCl) were weighed to calculate the mass of entrained K and Cl inside the centrifuge tubes.
3. Displacement of adsorbed K and Cl by ammonium nitrate: Twenty milliliters 1 N ammonium nitrate were added to the centrifuge tubes which were shaken for 1 h to displace the adsorbed K and Cl ions. After centrifuging at 48,000 RCF for 20 min, the solution was aspirated into 60 mL bottles. The displacement by ammonium nitrate was repeated twice and the extracts pooled. The concentration of K and Cl extracted by 1 N ammonium nitrate solution was measured. Potassium ions were measured by atomic absorption spectrometry (Instrumentation Laboratory, Lexington, Massachusetts, USA) and Cl ions were measured by a chloridometer (Haake Buchler Instruments, Saddle Brook, New Jersey, USA).

The adsorption of K and Cl ions by BC was calculated using the following equation:

$$\mathrm{K\ or\ Cl} = n_{\mathrm{K}}\ (\mathrm{or}\ n_{\mathrm{Cl}}) - M_{\mathrm{entr}} m_{\mathrm{k}} (\mathrm{or}\ M_{\mathrm{entr}} m_{\mathrm{cl}}) \quad (2)$$

where n_{K} or n_{Cl} was the K and Cl determined in 1.0 N ammonium nitrate (in step 3). M_{entr} denotes the mass of entrained solution left in the centrifuge tube before ammonium nitrate replacement (in step 2), and m_{K} or m_{Cl} denotes the concentration of K or Cl ions in the supernatant (in step 2). Surface positive charge was defined as the adsorption of anions (Cl^{-}), and surface negative charge was the adsorption of cations (K^{+}).

In this study, surface charge of BC was represented on a C basis (mmole kg C^{-1}). A quadratic model was used for fitting surface charge and pH. Point of zero net charge (PZNC) was defined as the pH that had an equal amount of surface positive and negative charge. Anion exchange capacity (AEC) was defined as the amount of net surface positive charge at pH 3.5; effective cation exchange capacity (ECEC) was defined as the amount of surface negative charge at BC's pH (under H_2O or 1 N KCl suspension); and potential cation exchange capacity (PCEC) was defined as the amount of surface negative charge at pH 7.

2.6. Relationships between BC oxidation and the climatic and soil characteristics

Simple linear correlations between BC oxidation and the climatic and soil characteristics were conducted for examining if the properties of historical BC were related to climatic and soil characteristics. Stepwise multivariate regressions (SAS 9.1, Proc Reg, SAS Institute, Cary, NC) confirmed the observations of these individual correlations. The examined parameters of BC oxidation included elemental C and O concentrations, atomic O/C ratios, PCEC, and ECEC at pH_{H_2O} and pH_{KCl}. The examined climatic and soil characteristics included MAT, MAP, effective precipitation (MAP – PET), soil pH, clay content, soil C/N ratio, and soil mineralized C as a proxi for microbial activity. Since the data from the XPS and FTIR measurements were qualitative rather than quantitative, these results were not included in the correlation model. In a separate study, it was shown that the BC-containing soils under conifer vegetation had higher C storage than the soils under broadleaf or grass vegetation (Cheng, 2008). Therefore, correlations between BC oxidation and the climatic and soil characteristics were only conducted for the sites under broadleaf and grass vegetation.

3. RESULTS

3.1. Elemental composition and molecular structure

New BC contained high amounts of C (90.8%) and low amounts of O (7.2%) and H (1.7%) (Fig. 1a and Table EA1). With coating of HA (BC-HA), very small decreases in C and increases in O were found, while aging of BC by incubation for 12 months showed a slightly higher reduction in C concentrations and increases in O and H concentrations. Carbon concentrations were reduced to 88.2% and 85.8%, while O concentrations increased to 9.2% and 10.6% and H concentrations to 2.4% and 3.4% for BC incubated at 30 °C (BC30) and 70 °C (BC70), respectively. In contrast, all historical BC samples displayed substantially decreased amounts of C and increased amounts of O and H. The average C concentration of historical BC samples was 70.5%, and average O and H concentrations were 24.8% and 4.5%. Natural oxidation of BC concomitantly increased atomic O/C ratios, from 0.06 in new BC to 0.26 in historical BC, and H/C ratios, from 0.23 to 0.76 (Fig. 1b and Table EA1).

Except for BC-HA which demonstrated comparatively lower C and higher O, the elemental compositions obtained from XPS measurements had similar trends compared to the elemental analyses, in that new BC had higher C and lower O concentrations compared to historical BC (Table 2). High-resolution XPS C1s spectra further indicated that the increases of O were due to the formation of oxygen-containing functional groups. Our data also showed that higher oxygen-containing functional groups, as well as lower C and O contents, were found on BC surfaces compared to entire particles for the historical BC samples and the sum of all oxygen-containing functional groups of the historical BC samples were two times higher than that of surfaces and 60% higher than that of the entire particles of new BC.

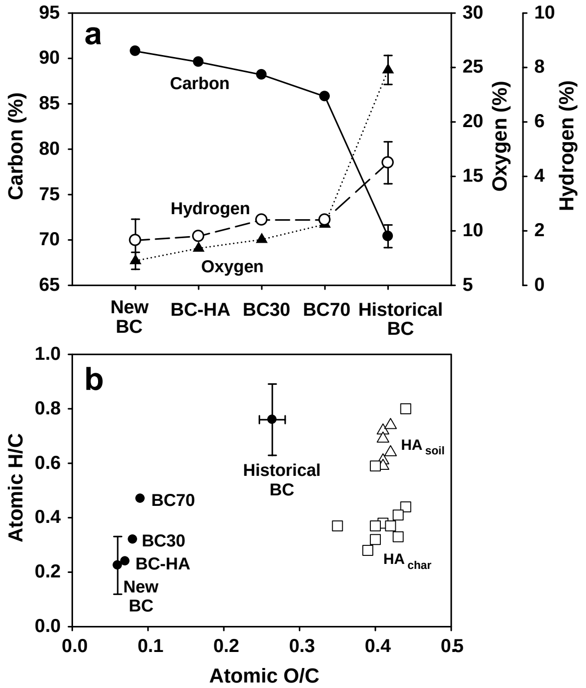

Fig. 1. (a) Elemental composition of carbon, oxygen and hydrogen; (b) atomic O/C versus H/C ratios (van Krevelen Diagram) of new ($n = 2$) and historical BC samples ($n = 11$). BC-HA represents the coating of new BC with HA. BC30 and BC70 denote aging of new BC under 30 and 70 °C for 12 months. HA_{soil} (open triangles, Haumaier and Zech, 1995) and HA_{char} (open squares, Trompowsky et al., 2006) represent the humic acid extracted from BC-rich soils and charcoal. Error bars represent 1 standard deviation.

The FTIR spectra of new BC, as well as BC-HA and BC30, showed a “flat” pattern and no bands were observed (Fig. 2). With progressive oxidation, the bands of functional groups evolved. The spectrum of BC70 showed discernable bands at wavenumbers of 1700 cm^{-1} and 1600 cm^{-1}. All historical BC displayed well resolved FTIR spectra (Fig. 2), with major bands at wavenumbers of 3400, 1700, 1600, 1585, 1380, and 1260 cm^{-1}. The band at 3400 cm^{-1} was assigned to OH bonds, 1700 cm^{-1} to carboxylic acid groups, 1600 cm^{-1} to molecular vibration of ring stretching in C=C, 1585 and 1380 $cm^{-1}$to carboxylate, and 1260 cm^{-1} to phenolic acid functional (C—O) and COOH groups (Starsinic et al., 1983; Guo and Bustin, 1998; Jia and Thomas, 2000).

Detailed FTIR measurements of QC and CT BC under different pH adjustments indicated that most bands of historical BC samples were pH dependent (Fig. 3). The band intensities at 1700 and 1260 cm^{-1} decreased with increasing pH; whereas the band intensities at 1585 and 1380 cm^{-1}increased with increasing pH. With the rise of pH values, the aromatic C=C band intensity at 1600 cm^{-1} was obscured by the increasing intensity of carboxylate bands at 1585 cm^{-1}. These results ascertained our band assignments.

Table 2
XPS widescan of the atomic compositions of carbon and oxygen and the deconvolution of C1s narrow scan spectra of new and historical BC samples

	Surface analyses								Bulk analyses							
	C (%)	Oc[a](%)	Oc/C	C1s composition (%)[b]					C (%)	Oc (%)	Oc/C	C1s composition (%)[b]				
				C=C	Sum[c]	C–O	C=O	COO				C=C	Sum[c]	C–O	C=O	COO
New BC																
New-BC$_{HW}$	91.3	8.7	0.10	77.5	22.3	15.4	3.6	3.3	ND	ND	ND	ND	ND	ND	ND	ND
New-BC$_{GW}$	90.2	9.6	0.11	77.2	22.9	14.5	4.5	3.9	ND	ND	ND	ND	ND	ND	ND	ND
BC-HA	84.0	14.5	0.17	71.0	28.9	19.3	4.6	5.0	ND	ND	ND	ND	ND	ND	ND	ND
BC70$_{6M}$[d]	86.5	13.0	0.15	71.2	28.8	19.9	4.1	4.8	ND	ND	ND	ND	ND	ND	ND	ND
Historical BC																
QC	61.1	30.5	0.50	50.5	49.5	25.9	17.0	6.6	77.3	21.1	0.27	67.8	32.2	16.1	8.8	7.3
NY	59.1	29.5	0.50	46.4	53.6	27.5	21.2	4.9	70.8	25.9	0.37	58.1	41.9	23.1	12.2	6.6
CT	ND	ND	ND	ND	ND	ND	ND	ND	69.7	25.8	0.37	61.4	38.6	17.6	12.2	8.8
OH	33.0	26.9	0.82	55.5	44.5	20.8	18.7	5.0	68.8	26.6	0.39	67.6	32.2	15.0	11.0	6.2
MD	51.3	27.4	0.54	49.3	50.7	28.1	16.4	6.2	75.0	23.5	0.31	65.2	34.8	17.1	10.1	7.6
TN	278	25.9	0.92	49.8	50.1	26.8	19.3	4.0	72.2	24.2	0.34	69.2	30.8	12.9	9.5	8.4
GA	30.6	34.0	1.11	46.5	53.6	29.1	20.5	4.0	67.7	28.2	0.42	62.2	37.9	17.9	11.5	8.5

ND, not determined.

[a] Oc: oxygen bound to carbon.

[b] The binding energy of C1s at 284.6 eV was assigned to C=C, C–C and C–H, at 286.2 eV to C–O, at 287.6 eV to C=O, and at 289.1 eV to O–C=O.

[c] Sum of oxygen-containing functional groups.

[d] Incubation of new BC at 70 °C for 6 months.

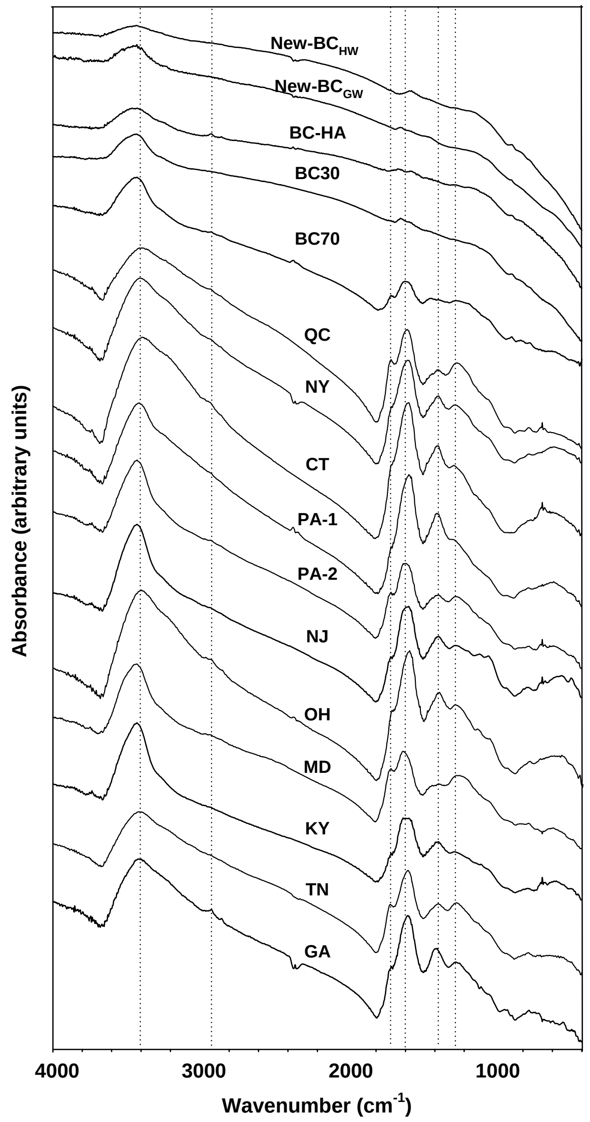

Fig. 2. FTIR spectra of new and historical BC samples. Flat spectra of new BC samples indicate absence of functional groups. With increasing oxidation of new BC, the band intensities are enhanced (BC70) and finally approach the well resolved spectra of historical BC. The band at 3400 cm^{-1} is assigned to OH bonds, 1700 cm^{-1} to carboxylic acid groups, 1600 cm^{-1} to molecular vibration of ring stretching in C=C, 1585 and 1380 cm^{-1}to carboxylate, and 1260 cm^{-1} to phenolic acid functional (C–O) and COOH groups.

3.2. Surface charge characteristics

The charge of most BC samples was strongly dependent on pH (Fig. 4). New BC had high amounts of surface positive charge (+71 mmole kg C^{-1} at pH 3.5), but very low amounts of surface negative charge (Table 3 and SI Table 2). With coating of HA (BC-HA), a slight decrease of positive charge and increase of surface negative charge were found, whereas aging of BC by a 12-month incubation caused greater alteration of surface charge than the coating of HA. Progressive oxidation of BC led to higher amounts

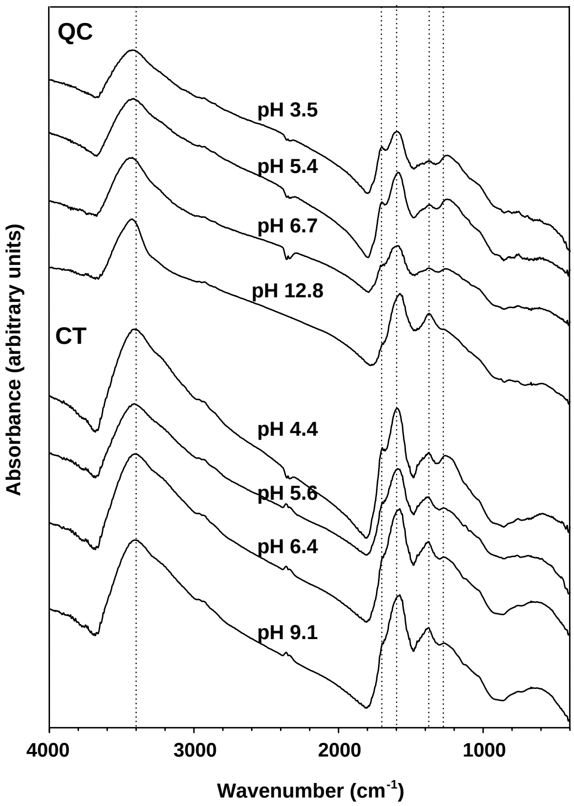

Fig. 3. FTIR spectra of the QC and CT BC samples at different pH values. Most bands are pH dependent and the band intensities at 1700 cm^{-1}(carboxylic groups) and 1260 cm^{-1} (carboxylic and phenolic groups) decrease with increasing pH, while the bands intensities at 1585 cm^{-1} (carboxylate) and 1380 cm^{-1} (carboxylate) increase with increasing pH.

of surface negative charge but lower amounts of surface positive charge, in which surface negative charge at pH 7.0 in BC70 was 201 mmole kg C^{-1} and BC30 was 71 mmole kg C^{-1} and surface positive charge in BC70 even diminished to zero. In contrast to new BC, all historical BC showed substantial amounts of surface negative charge and had an average surface negative charge of 1644 mmole kg C^{-1} at pH 7.0. At the same time, no positive charge existed in historical BC, which was similar to the results for BC70.

The PZNC of new BC was at pH 7.0 (Table 3). The PZNC of BC-HA slightly shifted to pH 6.8, while the PZNC dropped to pH 3.4 and 2.7 during aging of BC at 30 and 70 °C for 12 months, respectively. Similar to the aged BC, all historical BC samples showed acidic PZNC values of around pH 3.

3.3. Correlation between BC oxidation and climatic and soil characteristics

Of all climatic and soil characteristics examined, MAT was the best predictor for BC oxidation (Table 4, and Fig. EA1). Based on simple linear regression, MAT significantly explained 84% of the variability of C concentrations ($r = -0.92$; $P < 0.01$), 52% of the variability of O concentrations ($r = 0.72$; $P < 0.01$), 60% of the variability of atomic O/C ratios ($r = 0.78$; $P < 0.01$), and 69% of the variability of PCEC ($r = 0.83$; $P < 0.01$) (Fig. 5a). Thus, lower C concentrations and higher O concentrations, O/C ratios, and PCEC values were found for the BC samples from warmer areas. Effective CEC was significantly and positively correlated with soil pH, which explained 70% of the variability ($r = 0.85$ in average; $P < 0.01$), while no other correlation was found between pH and BC oxidation parameters. In addition, no other climatic or soil characteristic, such as MAP, effective precipitation (MAP-PET), C/N, clay content, or potential C mineralization, showed a significant correlation with BC oxidation.

MAT was better correlated with the Oc/C ratios of BC surfaces ($r = 0.97$; $P < 0.01$) than with the Oc/C ratios of entire BC particles ($r = 0.67$; $P > 0.05$; Fig. 5b). The Oc/C ratios of surfaces responded 7-fold stronger to increases in MAT than entire particles.

4. DISCUSSION

4.1. Natural oxidation of BC

Our data clearly indicate that historical BC samples, representing a wide variety of geographic environments, are substantially oxidized after 130 years of exposure to soil. The van Krevelen diagram demonstrates the fundamental pathway of natural oxidation of BC (Fig. 1b), and indicates that the processes of natural oxidation of increasing both atomic H/C and O/C ratios display an opposite trend from pyrolytic processes (Shindo, 1991; Baldock and Smernik, 2002). It is also interesting to note that the O/C ratios of humic acids extracted from charcoal (Trompowsky et al., 2006) and BC-containing soil (Haumaier and Zech, 1995) were significantly greater, while H/C ratios of soils were similar and H/C ratios of charcoal were lower than those of historical BC (Fig. 1b). Extracted humic acids from charcoal had an average H/C ratio of 0.5 and O/C ratio of 0.4 (Trompowsky et al., 2006), and BC-rich soils had an average H/C ratio of 0.67 and O/C ratio of 0.41 (Haumaier and Zech, 1995). Therefore, extractable HA from BC appeared to be more oxidized than the particulate BC studied here.

The differences between surface and bulk properties by XPS measurements highlight the fact that higher oxidative states were found on the surface region of BC particles relative to the interior (Brodowski et al., 2005; Lehmann et al., 2005; Liang et al., 2006). For the field BC samples, however, it is still difficult to unambiguously distinguish whether surface oxygen functional groups were due to adsorption of non-BC or the oxidation of BC itself. In our study, the significant relationship between MAT and surface atomic O/C ratios may suggest a significant contribution from surface oxidation of BC itself rather than adsorption of non-BC (Fig. 5b). The lower increase in oxidation and PCEC by coating with HA than short-term incubation points in the same direction. On the long term, the exposure of BC in soils still resulted in considerable penetration of BC oxidation into the interior compared to new BC samples.

The flat FTIR spectrum of new BC implies that the functional groups were completely eliminated during the charring processes (Nishimiva et al., 1998). With the oxidation of new BC, the band intensities were enhanced through the introduction of dipole moments from forming functional groups (Starsinic et al., 1983; Morterra et al., 1984) and finally approached a well resolved spectrum, as shown by historical BC. The distribution of bands for the different

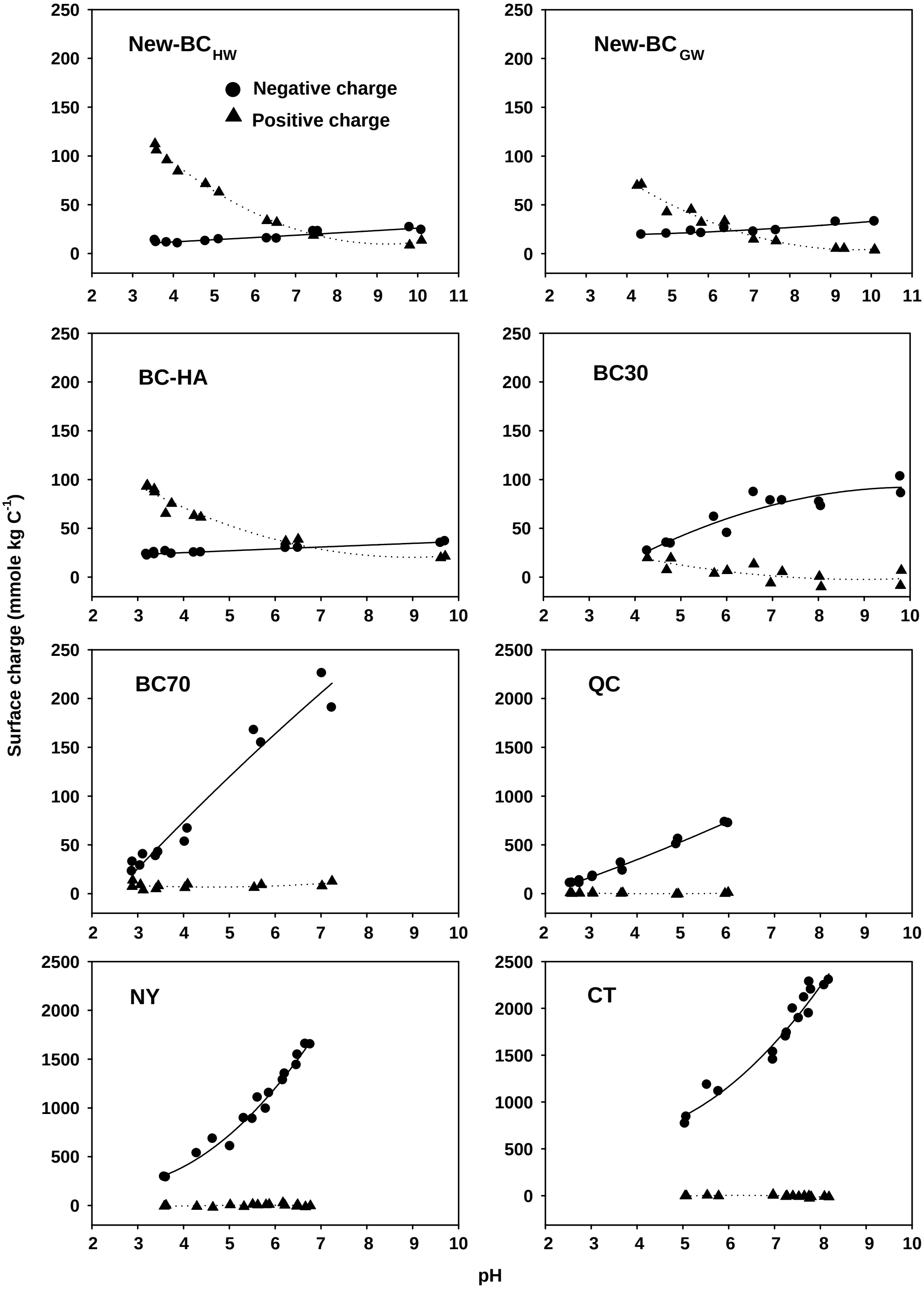

Fig. 4. The values of surface positive charge (triangles) and surface negative charge (circles) versus pH of new and historical BC samples. Quadratic regressions for surface positive charge and surface negative charge are shown with dotted and solid lines, respectively. Point of zero net charge (PZNC) is the pH of the intercept point between negative and positive charge curves. With progressive oxidation, positive charge decreases, negative charge increases, and PZNC shifts from pH 7 in new BC to pH 3 in historical BC. Note the different scale of the y axes between new and historical BC samples.

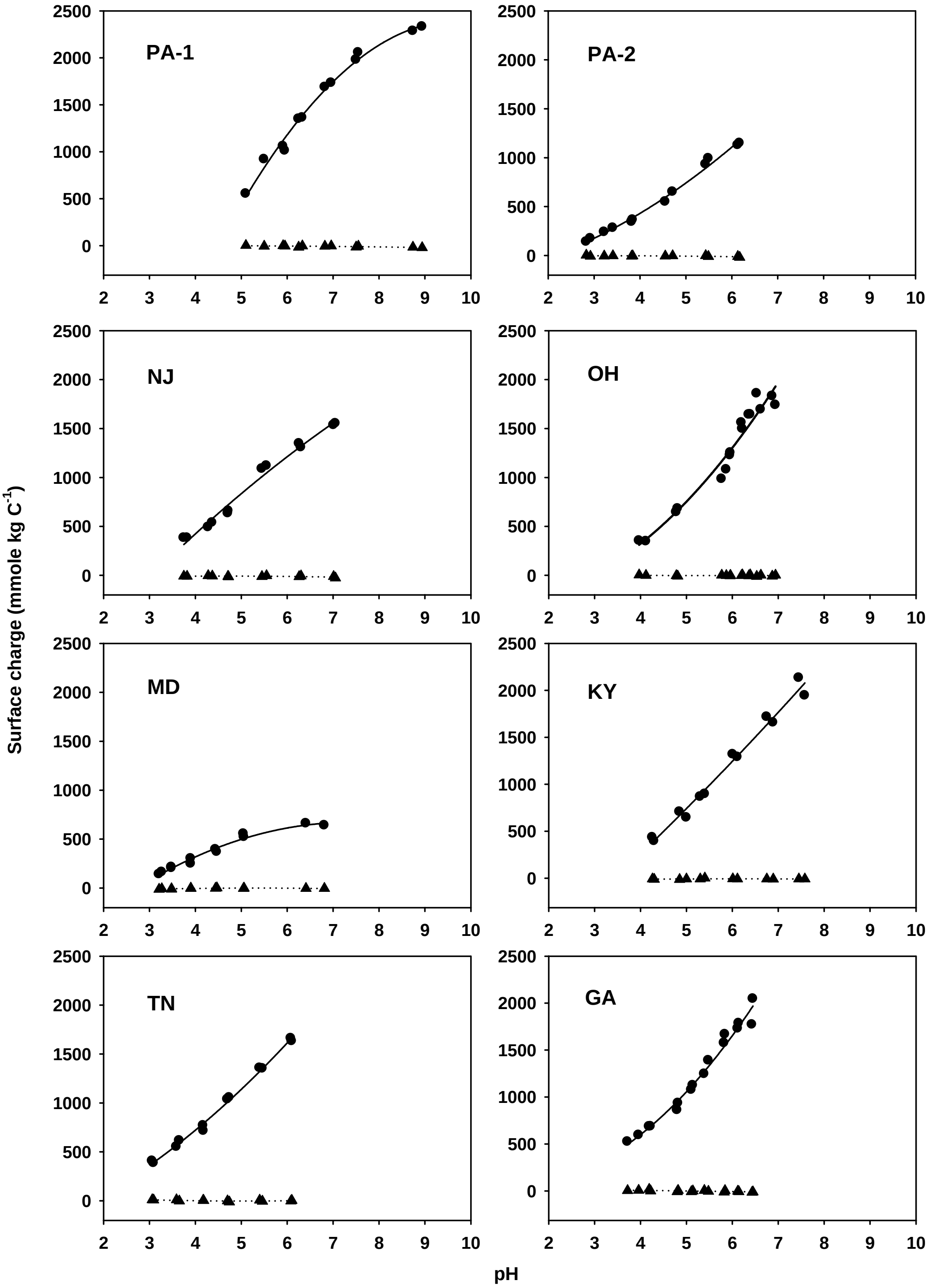

Fig. 4 (*continued*)

historical BC samples and therefore the main functional groups were similar, even though the BC samples were collected from different locations. Our results from XPS and FTIR directly indicate that the increase of O was not merely an adsorption of O to BC surfaces but a formation of oxygen-containing functional groups through natural oxidation of BC (Puri, 1970; Boehm, 1994). FTIR spectra suggest that carboxylic and phenolic functional groups were the dominant functional groups in the historical BC samples.

Formation of functional groups provides sites for surface negative charge. With progressive oxidation, surface negative charge of BC concurrently increased. Unlike new BC which contained AEC, both BC incubated at 70 °C and historical BC always exhibited CEC at any pH values above pH 3. Although aging of new BC at 70 °C for 12

Table 3
Point of zero net charge (PZNC), surface positive charge (AEC), effective cation exchange capacity (ECEC), potential cation exchange capacity (PCEC) of new BC and historical BC samples

	PZNC	AEC $pH_{3.5}$ (mmole kg^{-1} C)	PCEC $pH_{7.0}$ (mmole kg^{-1} C)	ECEC pH_{H_2O} (mmole kg^{-1} C)	ECEC pH_{KCl} (mmole kg^{-1} C)
New BC	7.1 (0.5)[a]	+84[b] (20.7)	+1.7 (9.7)	9.5 (3.1)	9.2 (3.6)
BC-HA	6.8	+58	2	+10	+6
BC30	3.4	+18	71	85	83
BC70	2.7	Nil	201	173	77
Historical BC	2.8 (0.6)[a]	Nil	1644 (504)	1125 (424)	668 (410)

[a] Standard deviation ($n = 2$ for new BC; $n = 11$ for historical BC).
[b] +: net positive surface charge at the assigned pH value.

Table 4
Correlation coefficients between BC properties and the corresponding climatic and soil characteristics ($n = 9$)[a]

	C	O	Atomic O/C	PCEC[b] $pH_{7.0}$	ECEC[c] pH_{H_2O}	ECEC[c] pH_{KCl}
MAT	−0.92[f]	0.72[f]	0.78[f]	0.83[f]	0.50	0.29
MAP	−0.52	0.41	0.44	0.37	0.00	−0.05
MAP-PET	0.37	−0.27	−0.29	−0.50	−0.54	−0.31
Soil pH_{H_2O}	0.09	−0.22	−0.33	0.11	0.87[f]	0.89[f]
Soil pH_{KCl}	−0.02	−0.35	−0.23	0.21	0.73[f]	0.91[f]
Soil C/N	0.13	−0.34	−0.30	−0.04	0.08	0.10
Silt	−0.29	0.63[e]	0.57	0.09	−0.47	−0.58
Clay	−0.58	0.54	0.55	0.43	−0.04	−0.03
C_{min}[d]	0.01	0.17	0.14	0.04	−0.06	0.02

[a] PA-2 and MD sites were not included in the model due to different vegetation types.
[b] PCEC: potential cation exchange capacity.
[c] ECEC: effective cation exchange capacity.
[d] C_{min}: potential cumulative mineralized C (g C—CO_2 per kg soil) for a 20-day incubation at 30 °C.
[e,f] Significant correlation at *P*-value 0.05 and 0.01, respectively.

months yielded a significant amount of CEC, the values were still much lower than by long-term natural oxidation as shown for the historical BC samples, which contained one order of magnitude greater CEC.

Concomitant to the increase of surface negative charge, surface positive charge decreased with progressive oxidation of BC and eventually disappeared. Similar results of decreasing surface positive charge through oxidation were also reported by Weller and Young (1948) and Papirer et al. (1987). Since the incorporation of O can localize π electrons and reduce the capability of anion adsorption (Leon y Leon et al., 1992), the decline of positive charge and the shift of PZNC to lower pH occurred rapidly and was even faster than the massive buildup of surface charge. In our study, for example, AEC and PZNC of BC incubated at 30 °C rapidly dropped from 84 mmole kg C^{-1} for New-BC_{HW} to 18 mmole kg C^{-1} and from pH 7.1 to pH 3.4, respectively; while PCEC only increased from +1.7 to 71 mmole kg C^{-1}. These values were much lower than the high CEC values when fresh BC was incubated at 70 °C or the CEC values of historical BC samples.

4.2. Adsorption of non-BC materials

With the coating of new BC by HA, surface negative charge slightly increased and surface positive charge and PZNC slightly decreased. Similar results have also been reported by Rivera-Utrilla et al. (2001). However, our data showed that the extent of change of BC properties by coating with HA were significantly lower than those by the oxidation of BC itself, especially compared to oxidized BC samples, such as BC70. From a long-term perspective, oxidation of BC itself was therefore more likely to influence BC properties rather than the adsorption of non-BC materials.

4.3. Effects of climatic and soil characteristics on BC oxidation

To our knowledge, this study is the first to compare the temperature dependence of long-term BC oxidation in soils across a wide geographic range. Although the long duration of time is an important cause for the high level of natural oxidation of BC, BC oxidation is significantly related to increasing MAT. Our data even suggest that temperature had a greater effect on BC oxidation than the time of exposure to soil. Enhanced BC oxidation (Puri, 1961; Cheng et al., 2006) and irreversible chemisorption of oxygen by char (Allardice, 1966) at higher temperatures have been reported in laboratory experiments and coincide well with our results on the natural oxidation of BC in soils. Our study further indicates that higher MAT increased the surface negative charge by 87 mmole kg C^{-1} for each degree Cel-

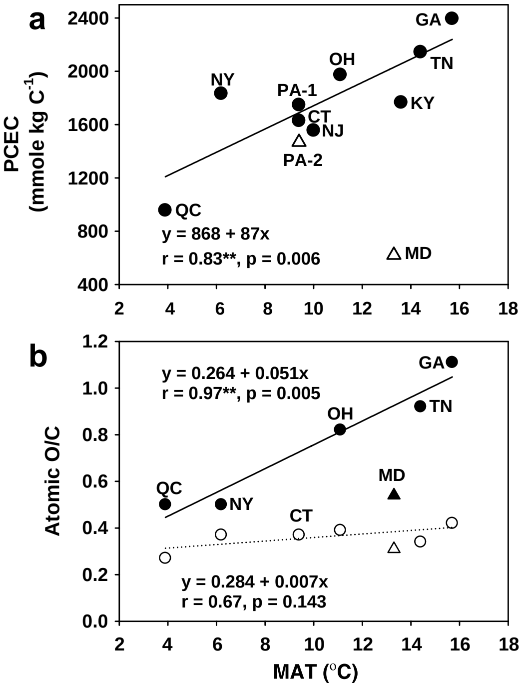

Fig. 5. (a) The relationship between mean annual temperature (MAT) and potential cation exchange capacity (PCEC) ($n = 9$); (b) the relationship between MAT and atomic O/C ratios measured by X-ray photoelectron spectroscopy (XPS) ($n = 6$), for surface (filled circles) and bulk data (open circles) of the historical BC samples. Triangles in both (a) and (b) denote sites under conifer vegetation (PA-2 and MD), which were excluded from the regression.

sius (Fig. 5a) and CEC ranges from 956 mmole kg C^{-1} in Quebec to 2354 mmole kg C^{-1} in Georgia. This very large negative charge is related to an oxidation of surfaces of BC which increases with greater temperature but has much lower effects on entire BC particles (Fig. 5b).

In contrast to the general understanding of weathering of mineral matter in soil which results in greater surface positive charge and higher PZNC with greater MAT as exemplified in tropical soils (Marcano-Martinez and McBride, 1989; Chorover and Sposito, 1995), higher MAT enhanced surface negative charge and oxidation lowered PZNC of BC. Since considerable amounts of CEC can be generated by BC, the presence of BC can even exceed the AEC in tropical soils. Consequently, high CEC was reported in tropical BC-containing soils, despite the fact that these soils contained highly weathered minerals (Liang et al., 2006).

The ECEC of the historical BC samples was positively correlated with pH values. These observations reinforce the findings that BC contains pH-dependent variable charge and that the in-situ ionization of BC directly depends on soil pH values. In archaeological research, Cohen-Ofri et al. (2006) found that self-humification of BC can be accelerated in soils with basic environments. However, it was not observed that pH influenced molecular structure and potential surface charge of BC, since there was no relationship between pH and the parameters of BC oxidation in our data set. The furnace sites of PA-2 and MD under conifer vegetation excluded from our calculation may require further investigation for their low oxidation and low pH values in order to understand the possible direct and indirect effects of pH and vegetation types on BC oxidation.

Although occlusion of small BC particles (<250 μm) inside aggregates or interactions with mineral surfaces were suspected to reduce BC oxidation (Glaser et al., 2000; Brodowski et al., 2005), no correlation was found between soil texture and BC oxidation in this study. This disparity may be due in part to the large size of BC fragments used in this study, which may reduce the interactions between BC and minerals. However, it is more likely that the wide range of MAT studied in this experiment masked the effects of soil texture on BC oxidation, and that a targeted research design is required to study soil texture effects. In addition, there was no correlation between soil organic matter quality or potential biological activity, such as soil C/N ratios and potential C mineralization, and BC oxidation. This finding may indicate that microbiological activity was not controlled to a different extent by substrate quality between BC-containing soils at different MAT. Differences in oxidation can then be explained by MAT and may not be limited by substrate quality.

4.4. Environmental significance

In natural ecosystems, evolution of negative charge may be an important ecological change of BC after forest or savanna fires. Annual BC production is estimated to be 50–270 Tg yr^{-1}, with a major source coming from vegetation fires (Kuhlbusch and Crutzen, 1995; Forbes et al., 2006). Unlike the BC samples used in this study that were produced at high temperature (>500 °C) (Hollingdale et al., 1999), BC from vegetation fire is generally produced at lower temperature (below 450 °C) (Chandler et al., 1983). Puri (1961) proposed that oxidation rates increase for BC produced at lower charring temperatures. It can be anticipated that most naturally produced BC should undergo more rapid oxidation than the BC samples used in this study.

Through natural oxidation in soil, the purposeful application of BC (often called biochar in this context) may evolve into a management tool to increase nutrient retention (Lehmann, 2007a,b). Production temperatures of about 450–600 °C reached in modern pyrolysis facilities for bioenergy and concurrent biochar production are similar to the ones reported for traditional kilns, and the information obtained from the present experiment provides guiding principles for the behaviour of biochar when applied to soil (Lehmann, 2007a,b). Lehmann et al. (2003) showed that BC-containing soils decreased the leaching of applied ammonium and that leaching of Ca was lower despite greater plant availability of Ca. High CEC is also an important reason for the high soil fertility in Amazon Dark Earths (Terra preta), where BC was deposited in pre-Columbian periods (Glaser et al., 2001). However, the relatively low oxidation and PCEC of incubated BC in comparison to 130-year old BC (this study) as well as the BC of Dark Earths with ages of up to several thousand years (Liang et al., 2006) still bears the question what the minimum time and temperature conditions are that generate high CEC on BC.

BC persists in soils for long periods of time, typically showing radiocarbon ages that are older than the most stable non-BC fractions in soils (Pessenda et al., 2001; Krull et al., 2006), and have been dated to originate from fire hundreds to thousands of years ago (Preston and Schmidt, 2006). Thus, BC found in soil is expected to be highly oxidized after such long-term exposure to natural oxidation processes. Oxidation of BC through both short- and long-term natural oxidation may therefore play an important role in the global BC cycles and in the effects of BC on soil biogeochemistry.

5. CONCLUSION

This paper reports substantial oxidation of BC in soils over a 130 year period, greatly exceeding oxidation by short-term laboratory incubation or by adsorption of organic matter. The principle oxidation processes of BC included: (1) increase of O and H and decrease of C, (2) formation of O-containing functional groups, and (3) decrease of surface positive charge and evolution of surface negative charge. While oxidation of BC significantly increased over time, it was also significantly modified by temperature, increasing with higher MAT. However, the dynamics of the development of oxidation and exchange sites and temperature sensitivity over time periods of decades still remain unclear. Future research should also address in what way soil clay content, clay mineralogy and pH influences the dynamics and temperature sensitivity of BC oxidation.

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APPENDIX A. SUPPLEMENTARY DATA

Elemental composition and pH values of BC samples (Table EA1), surface charge values of BC (Table EA2) and the linear regression of BC properties and environmental factors (Fig. EA1) are presented as online supporting material. This material is available free of charge via the Internet at http://www.sciencedirect.com/science/journal/00167037. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2008.01.010.

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Mulching material tested	2003	2004	2005	2006	2007
Garden Bio-Film Black	x	x	x	x	x
Garden Bio-Film NF01U/P 15 mic (short-cycle crops) Blk				x	x
Garden Bio-Film NF803/P 12 mic (longer cycle crops) Blk				x	x
Garden Bio-Film NF803/P 15 mic (longer cycle crops) Blk				x	x
Kraft brown paper (26-lb.)	x				
Kraft brown paper (81-lb)		x			
Kraft brown paper (26-lb.) with linseed oil coating	x				
Kraft brown paper (26-lb.) with tung oil coating	x				
Kraft brown paper (26-lb.) with soybean oil coating	x				
Kraft brown paper (42-lb.) w/polyethylene coating		x			
Envirocare 1 (XP-4611W) Black		x	x	x	x
Envirocare 2 (XP-4611J) Black		x	x	x	x
LF 1 - Raisin tray plastic – highly sized, high wet strength			x		
LF 2 - Leaf bag paper – normally sized, high wet strength			x		
LF 3 – Raisin tray paper – highly sized, no wet strength			x		
LF 4 – Bag paper – normally sized, no wet strength			x	x	x
LF 5 – Hi STFI Liner – medium sized, medium wet str.				x	x
Black LF 5 – LF 5 coated with black carbon					x
Planters Paper – Kraft paper with black pigment			x	x	x
Black Plastic (polyethylene) - Control	x	x	x	x	x

Searching for Alternatives to Plastic Mulch

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Introduction

The first man-made plastic was unveiled by Alexander Parkes in 1862, and since then plastics have led to advances in medicine and healthcare, innovations in packaging and products, and have become common place in our homes, offices, schools and almost every walk of our lives. Plasticulture, the use of plastics in agriculture, began in the 1950s and includes plastic mulches, greenhouse plastic, pots and plug trays, as well as irrigation pipe and tape. Since its introduction into agriculture, plastic has contributed significantly to the economic viability of farmers worldwide. The use of plastic mulch has become a standard practice for all vegetable farmers who benefit from reduced evaporation, weed control, reduced fertilizer leaching and soil compaction, as well as elevated soil temperatures that promote earlier plant maturity.

Though very effective and affordable, plastic mulch has become an environmental management concern due to disposal issues. On-site disposal options such as open burning and on-site dumping are environmental liabilities, and recycling of dirty plastics is not an economically feasible option. The disposal option that most growers choose is the landfill. In 1999, almost 30 million acres worldwide were covered with plastic mulch. More than 185,000 of those acres were in the United States, and essentially all of this plastic entered the waste stream. An effective and affordable alternative to plastic mulch would contribute the same production benefits as plastic mulch and in addition would reduce non-recyclable and non-renewable waste. In 2003, we began to investigate alternatives to plastic mulch in vegetable production at the WSU Vancouver Research and Extension Unit.

Materials and Methods

Our study included six mulch treatments: Garden Bio-Film, brown paper, paper + linseed oil, paper + tung oil, paper + soybean oil, and black plastic (control). In this study we used end rolls of 26 lb. kraft paper, similar to what is used to make paper grocery sacks. End rolls are left over from industrial orders and their price varies seasonally. The purpose of the oil application is to reduce the rate of paper degradation in the field. It is unclear if certain oils may be more effective than others. A thin film of oil was applied evenly over the entire surface of the paper. Oil was sprayed onto the paper prior to laying the paper in the field so that the edges of the paper where there is contact with the soil (the most likely site of degradation) would be coated with oil.

The experimental design of this study was a randomized complete block with four replications. Plots were 10 feet long and one bed wide, with two rows of drip tape laid under the mulch treatments. Paper and plastic mulch were laid in the field using conventional mulch laying equipment (Figure 1). Garden Bio-Film was laid by hand as the product we received from the

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[1] Lydia Garth is a senior at Columbia River High School in Vancouver and she participated on this study as part of her senior science project.

manufacturer was packaged for home gardeners and was not compatible with our equipment. The manufacturer will package product for commercial use if there is demand. Two rows of six varieties of basil were planted in each plot on June 25 (Figure 2). We measured plant height and the quality of the mulches throughout the season, and we measured plant fresh weight and plant dry weight at harvest. In August and September, we measured air temperature under some of the mulch treatments.

Figure 1. Laying paper mulch with conventional mulch laying equipment; drip tape was laid at the same time in 2 rows under the mulch.

Figure 2. Basil planted in 2 rows 10 feet long per plot; drip tape was laid under the mulch along each row of basil.

Results and Discussion

In this study the six basil varieties differed significantly in height and weight, but there was no interaction between variety and mulch treatment. That is, all six basil varieties responded in the same manner to each mulch treatment. Therefore we will only discuss the effects of mulch treatments on basil in general.

Plant Height. Plant height (cm) was measured weekly in August. Plant height differed significantly among treatments, and the Garden Bio-Film mulch treatment resulted in taller plants throughout the growing season (Table 1). Plant height in all of the paper mulch treatments did not differ from plant height in the black plastic mulch treatment at any time. Additionally, the type of oil applied to the paper had no affect on plant height. Plant height under the black plastic mulch was low at the beginning of August but high at the end of August. The low plant height in early August may have been a result of high temperatures from late July through early August (temperatures during those 3 weeks were the highest all summer, up to 100 °F). In contrast, plant height under the paper plus soy oil was high at the beginning of August but low at the end of August (Figure 3). Plant height throughout the experiment declined in week two, likely because we followed common basil growing practices and pinched flowers each week to encourage foliage development. Removing the apical dominance in the plant induced lateral growth that resulted in heavier branches that were initially bent down, thus reducing the plant's height.

Table 1. Height of basil plants grown with 6 mulch treatments.

Treatment	5-Aug	12-Aug	20-Aug	26-Aug
Paper	23.2ab	16.9b	21.5b	23.5b
Paper + Tung	19.5ab	16.9b	21.3b	23.6b
Paper + Linseed	14.4b	17.3b	21.4b	23.4b
Paper + Soy	27.3ab	17.3b	21.6b	23.5b
Garden Bio-Film	29.4a	20.3a	25.0a	27.1ab
Black Plastic	17.4ab	20.0a	23.8ab	25.9ab
p Value	0.2012	0.0392	0.0667	0.1049

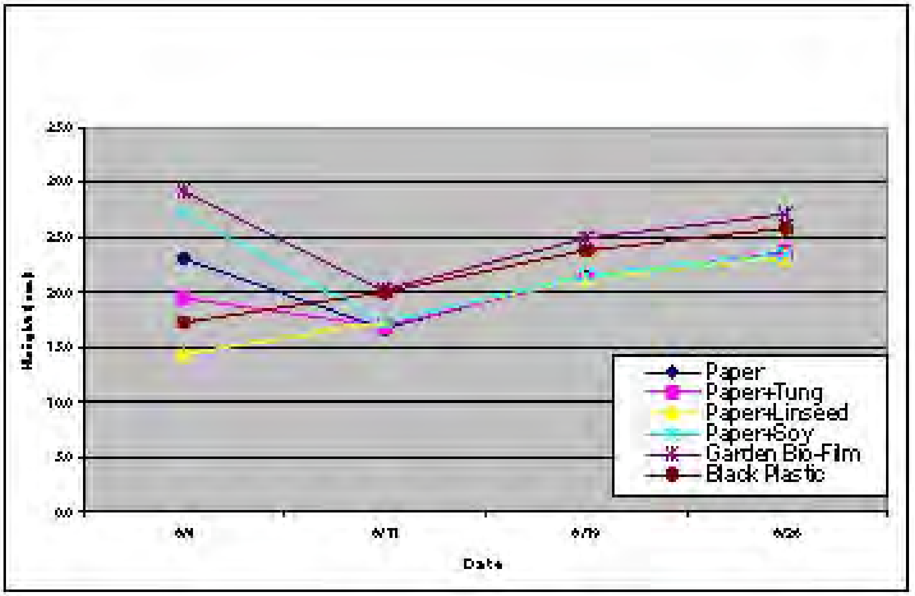

Figure 3. Height of basil grown with 6 different mulch treatments.

Plant Weights. Basil was harvested on August 25, and fresh and dry weights (g) were measured. Plant fresh weight and dry weight in the Garden Bio-Film mulch treatment tended to be the highest and weights in the black plastic treatment were second highest (Figure 4). However, these differences in fresh weight and dry weight were not significant (Table 2). Basil is a relatively short season crop and we harvested plants 8 weeks after transplanting. It is possible that a longer season crop would benefit more from the mulch treatments.

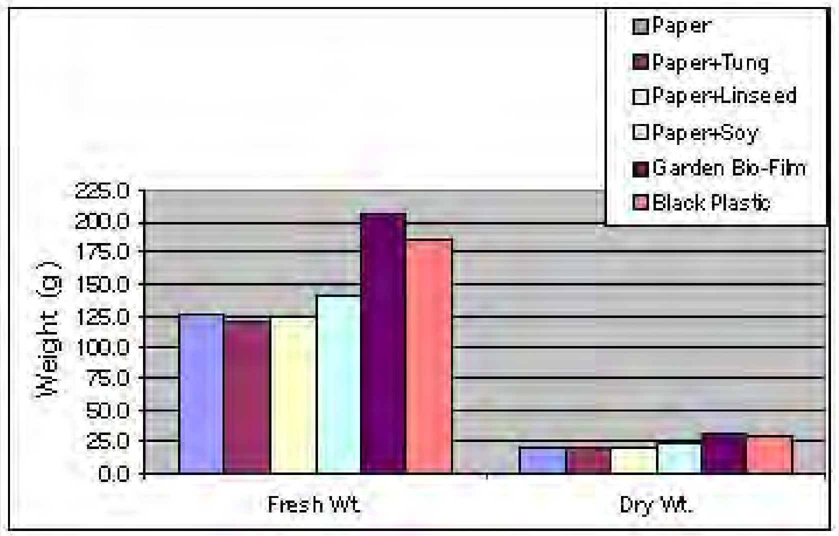

Figure 4. Fresh weight (g) and dry weight of basil grown with 6 mulch treatments

Table 2. Fresh weight (g) and dry weight of basil grown with 6 mulch treatments.

Treatment	**Field Wt**	**Dry Wt.**
Paper	126.0a	20.8a
Paper +Tung	118.9a	19.2a
Paper + Linseed	125.2a	20.5a
Paper + Soy	140.2a	23.7a
Garden Bio-Film	206.3a	32.1a
Black Plastic	185.9a	28.5a
p Value	0.4101	0.4173

Temperature. Temperature was measured under the paper (with no oil application) and the black plastic from August 6, and under the Garden Bio-Film from August 20 through September 3. We compared temperatures under the mulches to the temperature at the soil surface without mulch. Temperature fluctuated for each mulch treatment throughout the measurement period, so that no treatment consistently produced the highest or lowest temperature (Figure 5). From August 6 through August 12, temperatures were similar under the black plastic and paper mulches as compared to no mulch. From August 13 through August 21, day temperature where there was no mulch was approximately 5° F greater than under the paper mulch and 10° F greater than under the black plastic mulch. In general, the difference between day temperature and night temperature was greater where there was no mulch than for any of the mulch treatments.

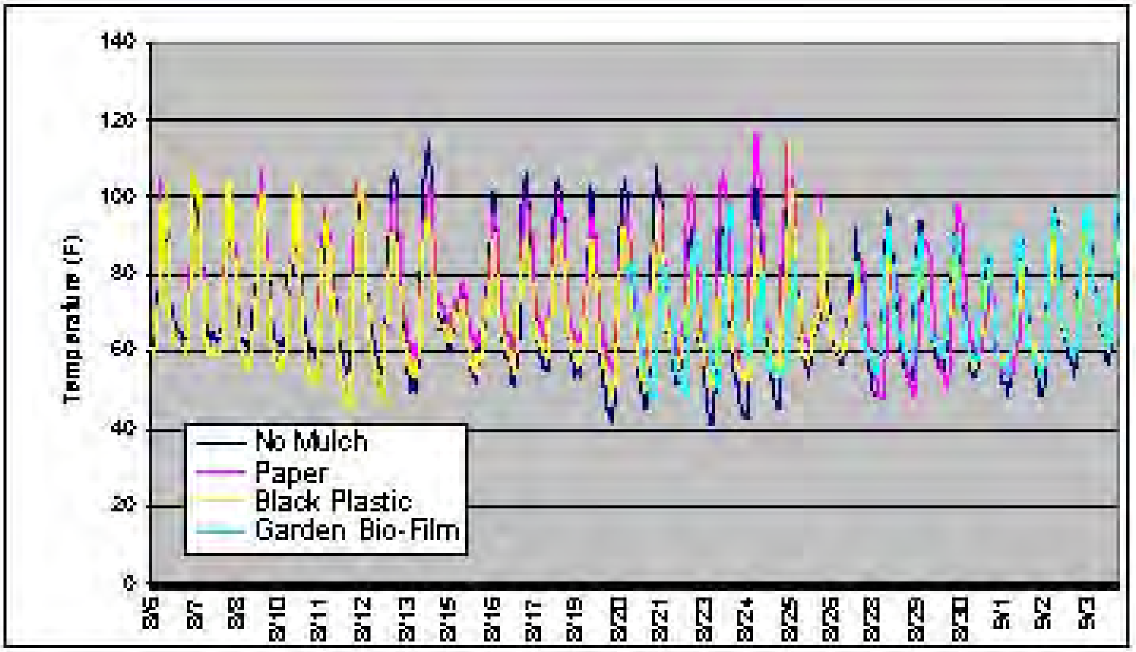

Figure 5. Temperature measured at the soil surface, under paper, black plastic, Garden Bio-Film and no mulch.

Mulch Quality. We rated mulches on a scale of 1-5 where 1 was completely disintegrated and 5 was completely intact. Ratings were based on the mulch's appearance including rips, holes, thin spots, water damage, mold, and weed growth. Ratings were done once a week throughout August. In this study there were no significant differences in mulch quality in the field due to the type of mulch. That is, all the mulches maintained their integrity throughout the study and weed control was excellent for all mulch treatments.

Garden Bio-Film and the black plastic mulches had the highest ratings on August 4 (4.4 and 4.0, respectively) while the paper mulches were all rated only slightly lower (3.6) (Figure 5). Garden Bio-Film steadily decreased in quality over the season and by August 25 was rated at 2.6, while black plastic only declined to 3.0 by the end of the study. Garden Bio-Film is designed to degrade in one growing season (90 days), thus the small rips and tears that we observed over the course of the study were normal. The Garden Bio-Film only began to partially degrade by the end of the study, but this did not affect plant growth or production, or weed control in this treatment.

The paper mulches, regardless of oil application, all had very similar and not significantly different ratings (3.0–3.6) throughout the experiment. Oil application had no effect on the quality of the paper mulch in the field over the course of this study. The paper we used in this study was 26 lb. and was thick and durable enough so that oil may not have been needed to increase its longevity. Or, we may not have applied sufficient oil to the paper to make a difference. The paper mulch, with or without oil, maintained its integrity and provided good weed control throughout the study.

It is important to note that much of the damage to the mulches that we observed was due to human error. Garden Bio-Film and the paper mulches were especially sensitive to any pressure or punctures caused by being walked on or poked with a hoe. Once damaged, the Garden

Bio-Film mulch ripped easily. The paper was only easy to damage when it was wet following irrigation. When the paper was dry, it did not puncture or rip easily. The papers sprayed with tung, linseed and soybean oil had a slight tendency to mold if they were damp on top, and this affected the quality and rating of the mulch. Having properly working drip irrigation and hot summers would eliminate this problem.

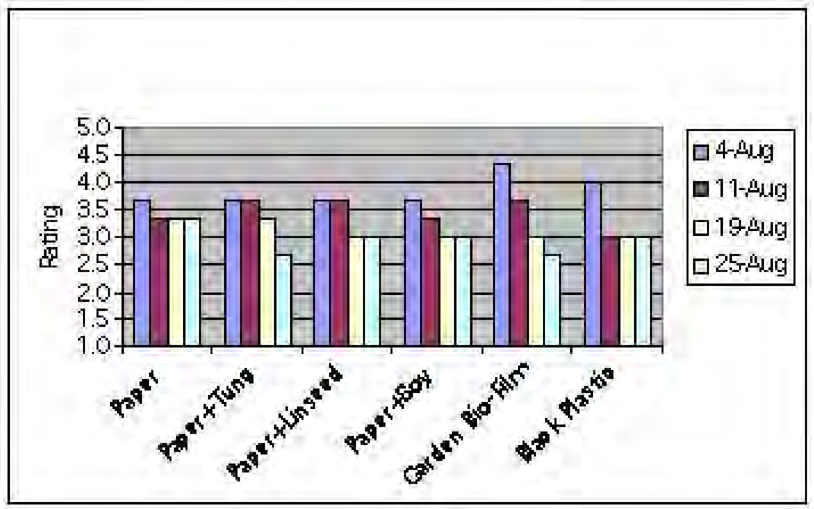

Figure 6. Ratings in the field of 6 mulches throughout August.

Conclusions

The purpose of this study was to determine if there are suitable alternatives to plastic mulch in regards to weed control and crop production in the Pacific Northwest. In this study we found that there were no differences in the quality or durability of the six mulch treatments or in the quality and yield of the vegetable crop. The oil had no effect on the longevity or qualities of the paper mulch. The paper mulches proved as high in quality as the plastic mulch and Garden Bio-Film. In adjacent observation plots, paper was laid in the field and then oils were applied. There was no difference in quality of the mulch whether oil was applied before or after laying the mulch in the field. In an additional adjacent observation plot, paper with no oil was laid in the field and overhead irrigation was applied throughout the summer. There was no difference in the quality of the mulch whether irrigation was applied through drip or overhead irrigation.

In 2004 we hope to continue to investigate alternatives to plastic mulch. We intend to test different weights of paper and we will again test Garden Bio-Film mulch. We will also evaluate the response of several types of vegetable crops to the different mulches. We will measure if crops that do best in high temperatures and crops that do best in cooler temperatures perform differently with the different mulches.

Sources of Mulch

Paper – Newark Paperboard Products
620 11th Ave, Longview, WA 98632
(360) 423- 3420
Attn: Jim McDaniel, General Manager

Garden Bio-Film – Biogroup USA, Inc.
107 Regents Pl. Ponte Vedra Beach, FL 32802
(904) 280-5094; Fax: (904) 543-8113; http://www.biogroupusa.com

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Takakura, T. and W. Fang. 2001. Climate under cover. Kluwer Academic Publishers p 1-10 <http://ecaaser3.ecaa.ntu.edu.tw/weifang/Bio-ctrl/cuc-chap1.pdf>

Alternatives to Plastic Mulch for Organic Vegetable Production

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Introduction. Weed control is one of the primary concerns in organic farming as it is labor intensive, expensive and time consuming. Since its introduction in the 1950s, plastic mulch has become a standard practice for many farmers to control weeds, increase plant growth, and shorten time to harvest, and has contributed significantly to the economic viability of farmers worldwide (Lamont, 1991; American Plastics Council, 2004). Though very effective and affordable, plastic mulch has become an environmental management concern due to disposal issues. On-site disposal options such as open burning and on-site dumping are environmental liabilities, and recycling of dirty plastics is not an economically feasible option at this time (Garthe, 2002). Recently, agricultural plastic recycling has begun, however, the disposal option that most growers choose is the landfill. In 1999, almost 30 million acres worldwide were covered with plastic mulch and more than 185,000 of those acres were in the United States (Takakura and Fang, 2001). Essentially all of this plastic entered the waste stream. An effective, affordable, degradable alternative to the now-standard plastic mulch would contribute the same production benefits as plastic mulch and in addition would reduce non-recyclable and non-renewable waste.

Previous work. In 2003, we conducted a preliminary study at Washington State University Vancouver Research and Extension Unit (WSU VREU) to evaluate paper and cornstarch mulches as alternatives to plastic mulch. We tested 81-lb Kraft paper with and without oil application. We evaluated three oils (soybean, linseed and tung) applied before and after laying the paper. Previous research found that Kraft paper treated with a combination of epoxidized soybean oil and citric acid held up for 13 weeks in the field and withstood wind and rain better than untreated Kraft paper (Shogren, 2003). A field evaluation study at the University of Florida found that watermelon grown on paper mulch coated with polymerized vegetable oil yielded on par with black plastic mulch (Hochmuth, 2001). In our study at WSU VREU, the paper mulch with and without oil proved as high in quality as the plastic mulch (Miles *et al.,* 2003). Though promising, further studies were needed to test different quality papers, additional mulch products and a diversity of vegetable crops.

Objectives. The purpose of this study was to identify degradable mulch products that can be used as effective and affordable alternatives to standard plastic mulch, and to then inform growers of the findings. We tested alternative mulches in an organic vegetable production system to evaluate their durability and effect on weed control, soil temperature and crop yield.

Methods. Black plastic and five alternative mulches were tested in an organic vegetable production system in 2004. The mulches were evaluated for durability and effect on weed control, soil temperature and crop yield. The mulch products included: 81-lb Kraft brown paper, 42-lb Kraft brown paper with polyethylene coating, Garden BioFilm, Envirocare 1 (XP-4611W), Envirocare 2 (XP-4611J), and 1 ml black plastic (control) (Table 1). Our field site was certified organic and managed accordingly. The experimental design was a randomized complete block with four replications. Plots were 50 feet long by 3 feet wide and each included four subplots, one for each vegetable crop. Lettuce (short season cool, variety "Pirat"), broccoli (long season cool, mixed varieties "Gypsy" and "Green Goliath"), and bell peppers (short season warm, variety "California Wonder") were planted in double 10-foot rows, while icebox watermelon (long season warm, variety "Smile") was planted in single 20-foot rows. The plots were drip irrigated, with drip tape laid beneath the mulch prior to planting. Each plot was rated bi-weekly for mulch quality. Vegetables were harvested at weekly intervals and measured to determine marketable yield, number of fruits or heads, plant biomass, and number of days to harvest. Beneath each mulch product, soil-surface temperatures were gathered throughout the study using Hobo field temperature monitors. The findings of this study are being disseminated to farmers and industry representatives through meetings, conferences, field days, newsletters, and our web site.

Durability. The mulch products evaluated in this study showed significant differences in quality over time (durability) (Table 2). The standard black plastic was the most durable mulch product in this study, with quality declining only slightly over the course of the growing season (Figure 1). The Envirocare mulches were the only products that compared to black plastic's durability. Envirocare 2 was still in very good condition at the end of the growing season and showed slightly better durability than Envirocare 1. Both Kraft paper mulches exhibited fair quality at the end of the season, but were significantly less durable than black plastic and Envirocare mulches. Garden BioFilm was the least durable, with a steadily declining quality rating throughout the season and was nearly completely degraded at the end of the growing season.

Days to first harvest. Crops were planted into the field as seedlings on June 24th, 2004. There was a significant difference among mulch treatments in the number of days to broccoli harvest, but all other crops were not significantly different (Table 3). Broccoli was harvested earliest from plots treated with Garden BioFilm, and latest from plots treated with black plastic. Lettuce was ready for harvest between 32 days (Envirocare 1) and 39 days (Envirocare 2) from transplant. Peppers were ready for harvest between 85 days (BioFilm) and 91 days (black plastic), and watermelon were ready from 80 days (Envirocare 1) to 88 days (Kraft 42).

Crop Yields. The different mulch products significantly affected broccoli and watermelon yields, but not yields of lettuce and pepper (Tables 4 & 5).

- **Lettuce:** Although lettuce yield was not significantly different due to mulch treatments, Envirocare 1 tended to produce the highest lettuce yield (kg) and Kraft 81-lb paper mulch produced the smallest yield. There was very little variability in number of heads produced by the different mulch treatments, therefore these slight differences in yield were due to head size.
- **Broccoli:** Broccoli yield (kg) and number of heads were significantly greatest in the black plastic mulch plots. Garden BioFilm and Kraft 81-lb paper produced large yields as well, while Envirocare 2 was the least productive in both yield and number of heads. There was no significant difference in average head weight.
- **Pepper:** There were no significant differences in pepper yield (kg), number of fruit and average pepper weight due to the different mulches. However, Garden BioFilm tended to produce the greatest yield (kg) followed by black plastic, while Kraft 81-lb paper tended to produce the lowest yield. The number of fruit tended to be highest with Envirocare 1 and lowest with Kraft

42-lb paper.

- **Watermelon:** Watermelon yields (kg) were significantly different due to the different mulch treatments. Envirocare 1 produced the largest yields and number of fruit while Kraft 81-lb produced the lowest. There were no significant differences in average fruit weight, therefore differences in overall yields were due to differences in fruit number.

Underlying Soil Temperature. Black Plastic mulch showed an insulating effect on underlying soil. That is, temperature highs and lows beneath the mulch were less extreme than above it (Figure 2). Temperatures under each mulch treatment in this trial were compared to temperatures under the black plastic (Figures 3-7). All of the mulches appeared similar to Black Plastic in their insulating effect, except for the Kraft 81-lb paper, which showed greater extremes of both high and low temperatures. This is probably due to the porosity of the Kraft paper material, but further studies would be needed to determine this.

Affordability. Approximate costs per acre were calculated for 80% mulch cover. Black plastic costs \$252 - \$281 per acre, and may differ depending on the source. Envirocare films are similar in price to black plastic, ranging from \$215 to \$243 per acre, and the coated Kraft 42-lb paper is also similar in cost, approximately \$235 per acre. The cost of Garden Bio-Film is higher, ranging from \$695 to \$1087, and the 81-lb Kraft Paper cost is variable depending on the source. The relatively heavy weight of paper makes shipping costs higher for paper mulches.

Conclusions. Results of this study indicate that there are alternatives to the standard plastic mulch that can produce comparable results in crop productivity, soil temperature, and affordability. Fully degradable mulches provide the added incentives of decreased work and decreased disposal costs because they do not have to be removed from the field. Preliminary results of this study indicate that Envirocare films are effective and affordable degradable alternatives to plastic mulch. They were comparable to black plastic in durability, crop yield, soil temperature, and affordability, and provide growers a choice between longer and shorter degradation times. However, the Envirocare films have not been approved to leave in the soil of certified organic systems, and therefore at this time must be removed. Further studies may be needed to determine the exact end products and possible residues of these films, so that they can be thoroughly reviewed for use in organic systems. Garden BioFilm has been approved for use in organic agriculture, and can be tilled into the soil. It produced good results in this study, and it's quick and thorough biodegradation may be desirable for short-season crops and immediate tillage into the soil, but the cost of this mulch is high, and it's rate of degradation may be too fast for longer-season crops. The paper mulches were less effective in general. Kraft 81-lb paper and K-aft 42-lb coated paper produced similar results in terms of yield and durability, but the Kraft 42-lb coated paper is not degradable and more labor-intensive to remove than black plastic. These results are preliminary, and this study will likely be repeated in 2005.

Future Work. This study to test degradable mulch products in organic vegetable production at WSU VREU will likely continue in 2005. New products become available each year, and in 2005 we hope to test an expanded number of mulch products. We will contact agricultural industry representatives, scientists, and farmers around the country to identify additional products that might be used as degradable alternatives to plastic mulch. Mulch treatments that we have identified so far include: 1) 81-lb Kraft paper, 2) Garden Bio-Film, 3) Envirocare black 1, 4) Envirocare white on black 1, 5) Envirocare black 2, 6) Envirocare white on black 2, 7) Bio-ground cover 1, 8) Bio-ground cover 2 and 9) black plastic (control). The greatest limitation we see to this work is finding degradable products that are approved to leave in the soil of certified organic systems.

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Takakura, T. and W. Fang. 2001. Climate under cover. Kluwer Academic Publishers, p 1-10 <http://ecaaser3.ecaa.ntu.edu.tw/weifang/Bio-ctrl/cuc-chap1.pdf>

MULCH SOURCES:

Envirocare 1 and 2: Pliant Corporation; 1475 Woodfield Road, Suite 700, Schaumberg, IL, 60173; 866-878-6188; www.pliantcorp.com

Garden Bio-Film: BIOgroupUSA, Inc., 107 Regents PI., Ponte Vedra Beach, FL 32082; 904-280-5094; www.biogroupusa.com

Kraft 81-lb Paper: Newark Paperboard Products; 620 11th Ave., Longview, WA, 98632; 360-423-3420; www.newarkgroup.com (*No longer available from this source)*

Kraft 42-lb Polyethylene-coated Paper: Graphic Packaging; 814 Livingston Court, Marietta, GA, 30067; 770-644-3000; www.graphicpkg.com

Black Plastic: from Peaceful Valley Farm Supply P.O. Box 2209, Grass Valley, CA 95945; (530) 272-4769; www.groworganic.com

SEED SOURCES:

“Pirat” Lettuce from Wild Garden Seed, www.wildgardenseed.com

“California Wonder” Peppers from Peaceful Valley Farm Supply, www.groworganic.com

“Smile” Watermelon from America Takii Seeds, www.takii.com

“Gypsy” and “Green Goliath” Broccoli, from Burpee, www.burpee.com

Table 1: Specifications of mulch products tested at WSU VREU in 2004.

Mulch Product	Composition	Degradability	Approved for use in organic systems?
Black Plastic	1.0 mil embossed film composed of high density polyethylene. Colored with carbon black pigment.	Not degradable.	Yes. Must be removed from the soil.
Envirocare 1, XP-4611W	Low-density and linear low density polyethylene, with Ciba Envirocare TDPA (Totally Degradable Plastic Additive). Contains no vinyl and no heavy metals. Colored with carbon black pigment.	Completely degradable. Thermal and photo triggers for degradation, beginning at 75 days. End products are CO2, H2O, and microbial biomass.	Yes. Must be removed from the soil.
Envirocare 2, XP-4611J	Low-density and linear low density polyethylene, with Ciba Envirocare TDPA (Totally Degradable Plastic Additive). Contains no vinyl and no heavy metals. Colored with carbon black pigment.	Completely degradable. Thermal and photo triggers for degradation, beginning at 140 days. End products are CO2, H2O, and microbial biomass.	Yes. Must be removed from the soil.
Garden BioFilm	Biodegradable black plastic film produced from cornstarch and other earth friendly resources. Contains no polyethylene.	Completely degradable. Begins degrading at 50-60 days, and is 95% degraded within 90 days.	Yes. Can remain in the soil.
42-lb Coated Kraft Paper	Brown paper coated with transparent polyethylene. (Commonly used for food packaging.)	Not completely degradable.	Yes. Must be removed from the soil.
81-lb Kraft Paper	Brown paper bonded with cement.	Completely degradable.	Yes. Can remain in the soil.

Figure 1: Mulch quality over time: Average rating of all replications per mulch product. Rated on scale of 0-9, where 0 is the worst and 9 is the best.

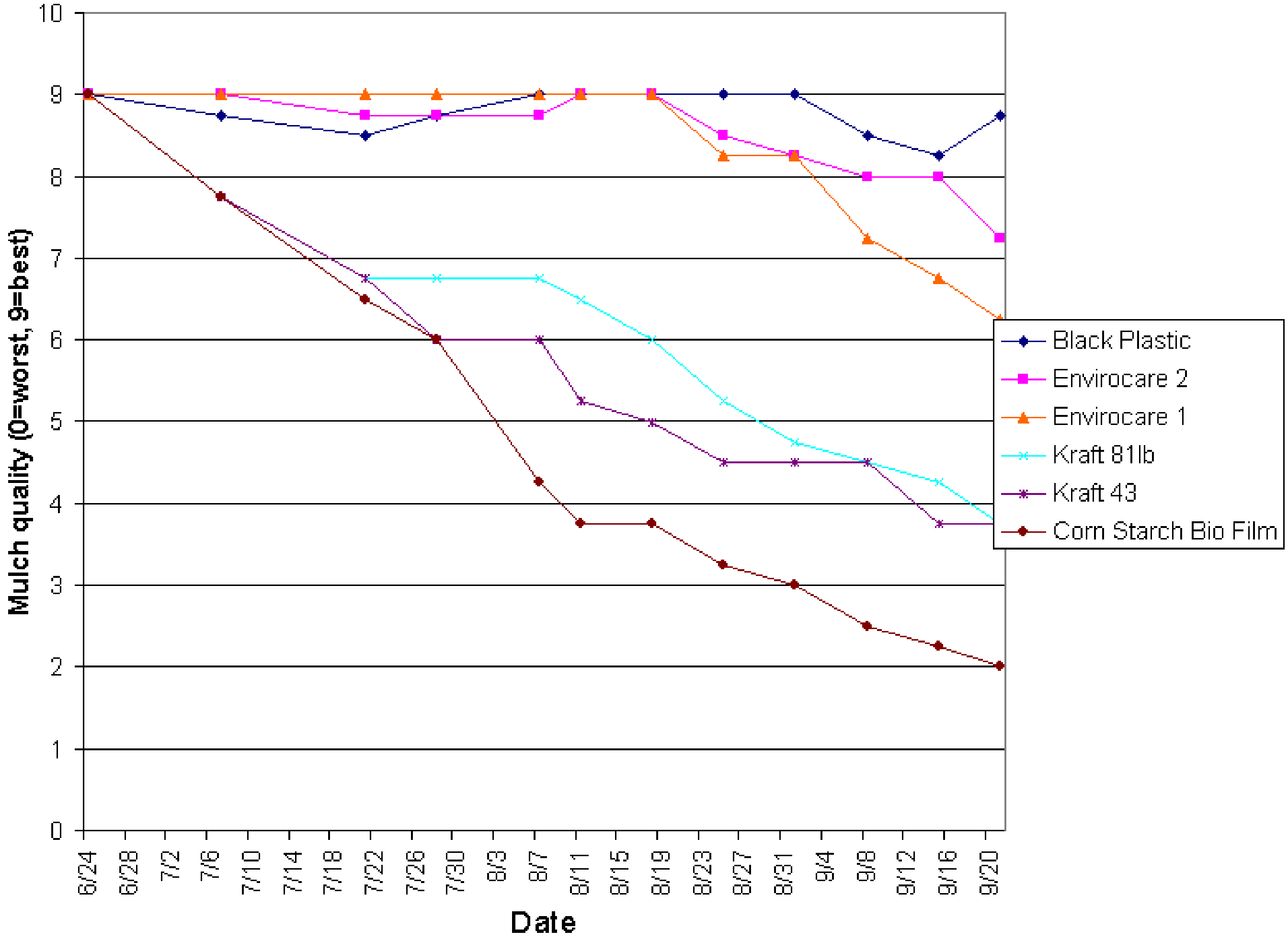


Table 2: Mulch quality over time: Average rating of all replications per mulch product. Rated on scale of 0-9, where 0 is the worst and 9 is the best.

Mulch	21-Jul	28-Jul	7-Aug	11-Aug	18-Aug	25-Aug	1-Sep	08-Sep	15-Sep	21-Sep
Black Plastic	8.5	8.8	9.0	9.0	9.0	9.0	9.0	8.5	8.3	8.8
Envirocare 1	9.0	9.0	9.0	9.0	9.0	8.3	8.3	7.3	6.8	6.3
Envirocare 2	8.8	8.8	8.8	9.0	9.0	8.5	8.3	8.0	8.0	7.3
Garden BioFilm	6.5	6.0	4.3	3.8	3.8	3.3	3.0	2.5	2.3	2.0
Kraft 42-lb	6.8	6.0	6.0	5.3	5.0	4.5	4.5	4.5	3.8	3.8
Kraft 81-lb	6.8	6.8	6.8	6.5	6.0	5.3	4.8	4.5	4.3	3.8
P Value = 0.0000										

Table 3: Mean number of days from transplant to harvest.

Mulch	Lettuce	Broccoli	Peppers	Watermelon
Black Plastic	33.9	75.9	91.2	84.5
Envirocare 1	32.5	67.4	89.2	80.4
Envirocare 2	35.4	70.8	89.4	82.6
Garden BioFilm	33.5	66.9	85.2	83.2
Kraft 42-lb	33.7	67.6	86.5	83.3
Kraft 81-lb	33.0	67.6	85.8	88.1
Mean	**33.7**	**69.4**	**87.9**	**83.7**
P Value	***0.5875***	***0.0687***	***0.3536***	***0.5414***

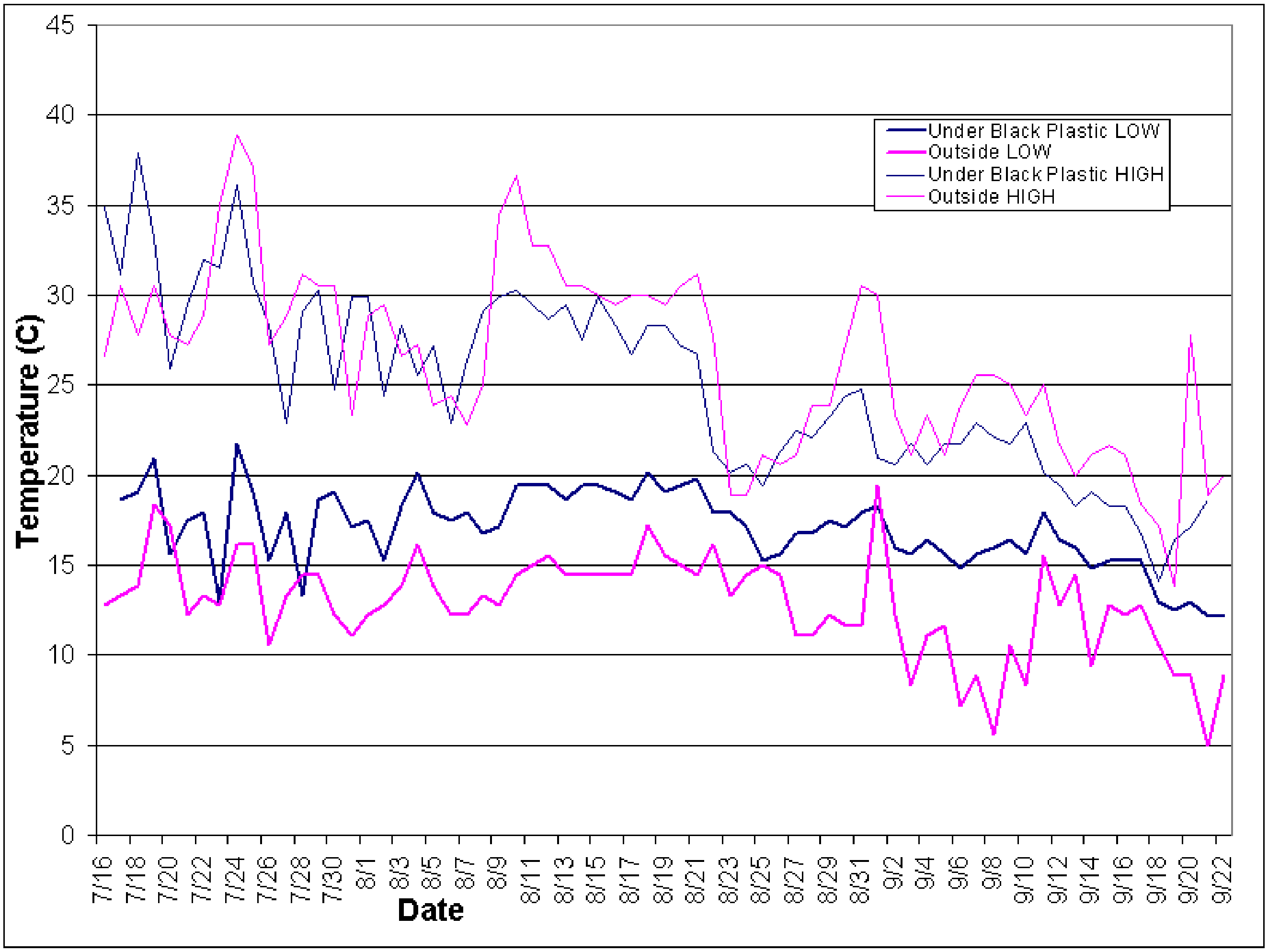
Table 4: Mean plot yield, average head weight, and number of marketable heads of Lettuce and Broccoli.

	LETTUCE						BROCCOLI					
Mulch	**Yield (kg)**		**Avg head wt. (kg)**		**No. of heads**		**Yield (kg)**		**Avg head wt. (kg)**		**No. of heads**	
Black Plastic	4.98	a	0.276	a	18.0	a	7.28	a	0.655	a	12.8	a
Envirocare 1	6.05	a	0.306	a	19.8	a	4.01	b	0.651	a	6.8	b
Envirocare 2	4.63	a	0.251	a	18.0	a	3.22	b	0.573	a	5.3	b
Garden BioFilm	5.03	a	0.252	a	19.8	a	4.78	ab	0.762	a	6.3	b
Kraft 42-lb	4.91	a	0.246	a	20.0	a	3.95	b	0.641	a	6.0	b
Kraft 81-lb	4.47	a	0.232	a	19.3	a	4.68	ab	0.684	a	7.0	b
P Value	**0.4588**		**0.2225**		**0.5945**		**0.1046**		**0.8605**		**0.091**	

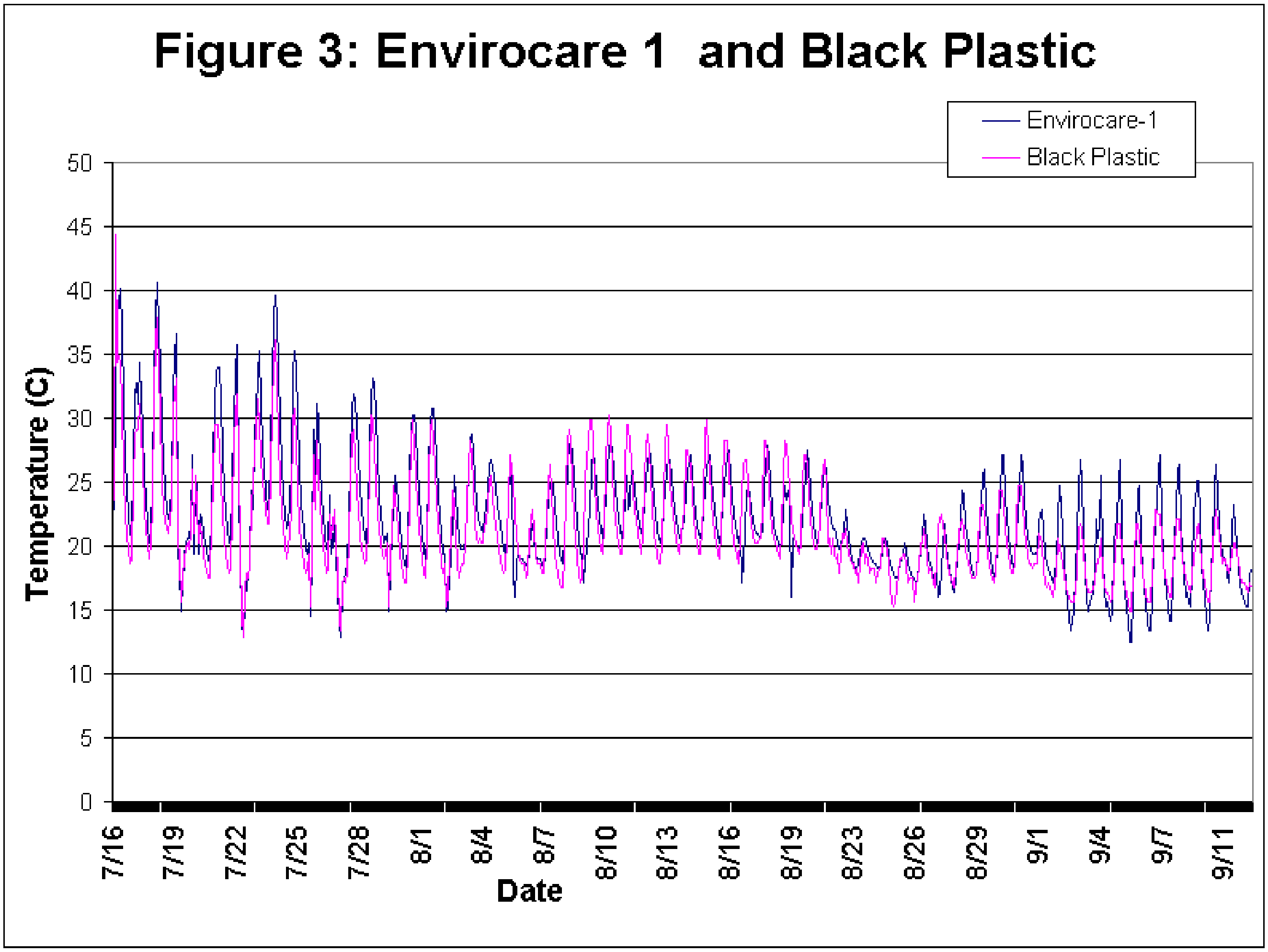
Table 5: Mean plot yield, average fruit weight, and number of marketable fruit of Pepper and Watermelon.

	PEPPER						WATERMELON					
Mulch	**Yield (kg)**		**Avg fruit wt. (kg)**		**No. of fruit**		**Yield**		**Avg fruit wt. (kg)**		**No. of fruit**	
Black Plastic	19.48	a	0.253	a	79.0	a	55.10	a	3.078	a	18.8	ab
Envirocare 1	14.60	a	0.178	a	82.0	a	71.15	a	2.925	a	24.0	a
Envirocare 2	13.44	a	0.175	a	77.3	a	50.37	ab	2.790	a	17.5	ab
Garden BioFilm	22.11	a	0.270	a	80.5	a	47.50	ab	2.953	a	16.3	abc
Kraft 42-lb	15.90	a	0.227	a	62.8	a	44.85	ab	3.245	a	13.8	bc
Kraft 81-lb	11.23	a	0.164	a	70.5	a	19.64	b	2.742	a	7.0	c
P Value	**0.6797**		**0.7115**		**0.5653**		**0.0650**		**0.5727**		**0.0307**	

Figure 2: High and Low Daily Temperatures Under Black Plastic Mulch and Outside



Figures 3-7: Temperatures under black plastic compared with temperatures under alternative mulch products.



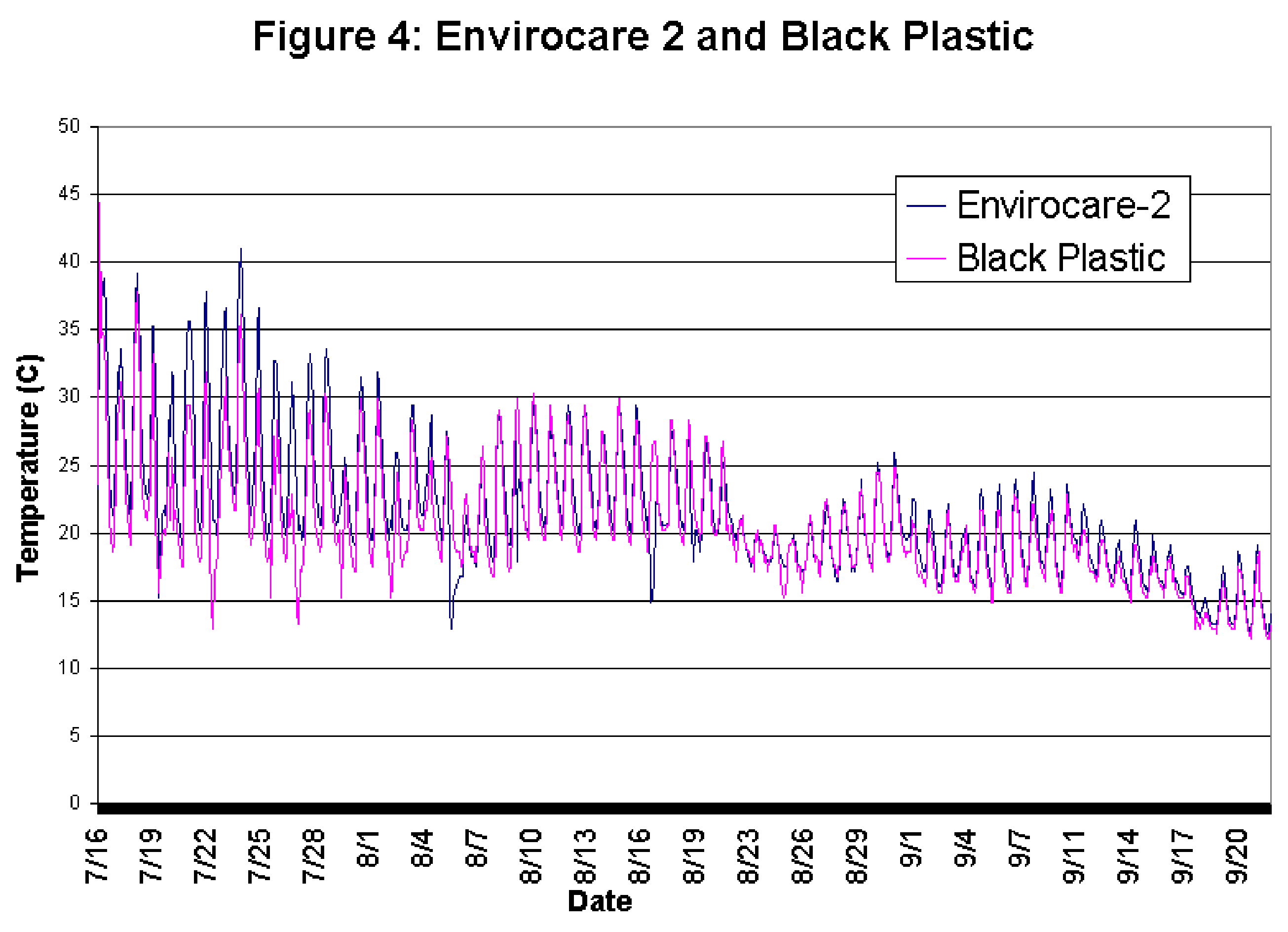


Figure 4: Envirocare 2 and Black Plastic
Temperature (C)
50
45
40
35
30
25
20
15
10
5
0
Envirocare-2
Black Plastic
7/16
7/19
7/22
7/25
7/28
8/1
8/4
8/7
8/10
8/13
8/16
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9/11
9/14
9/17
9/20
Date

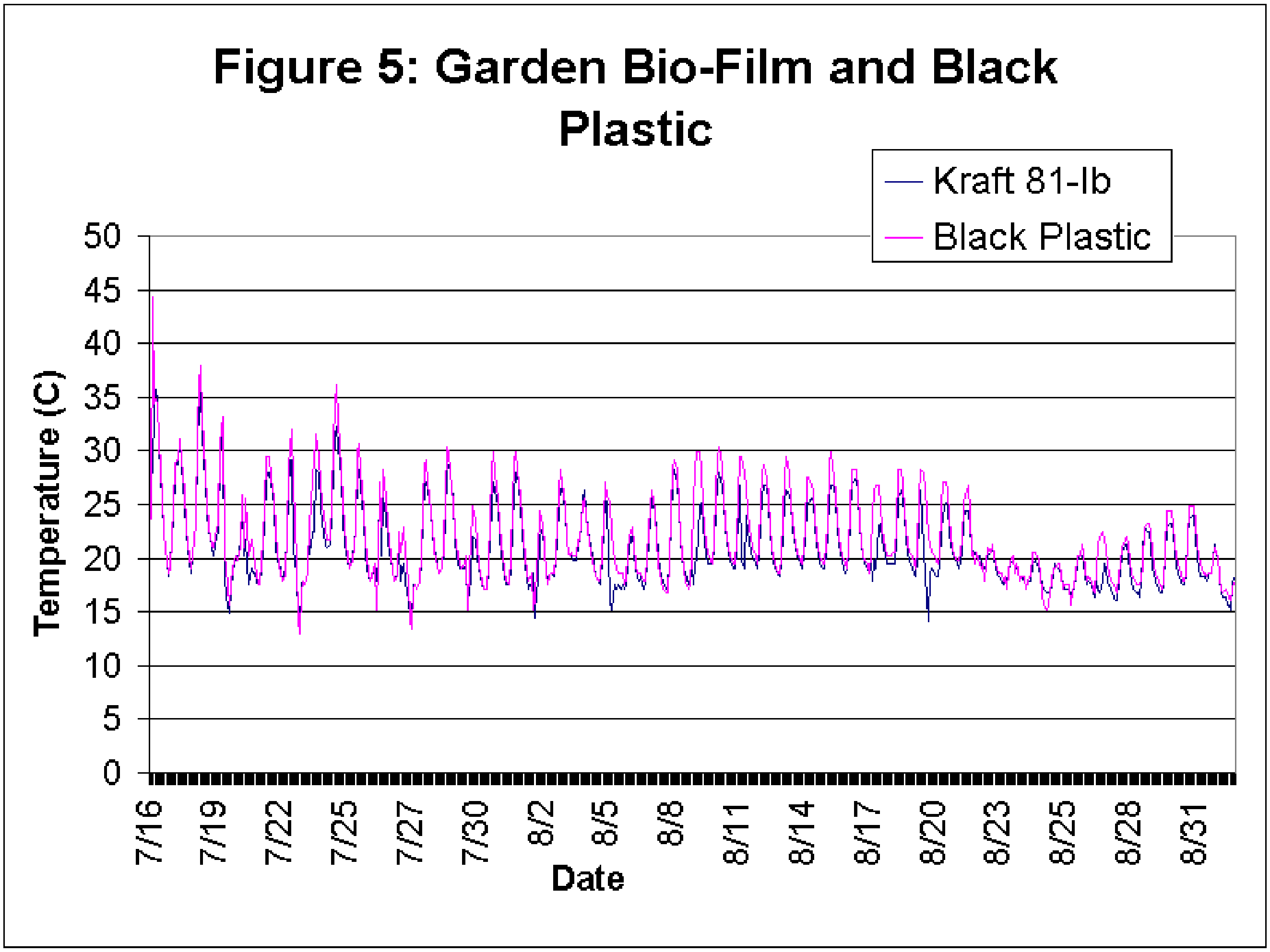
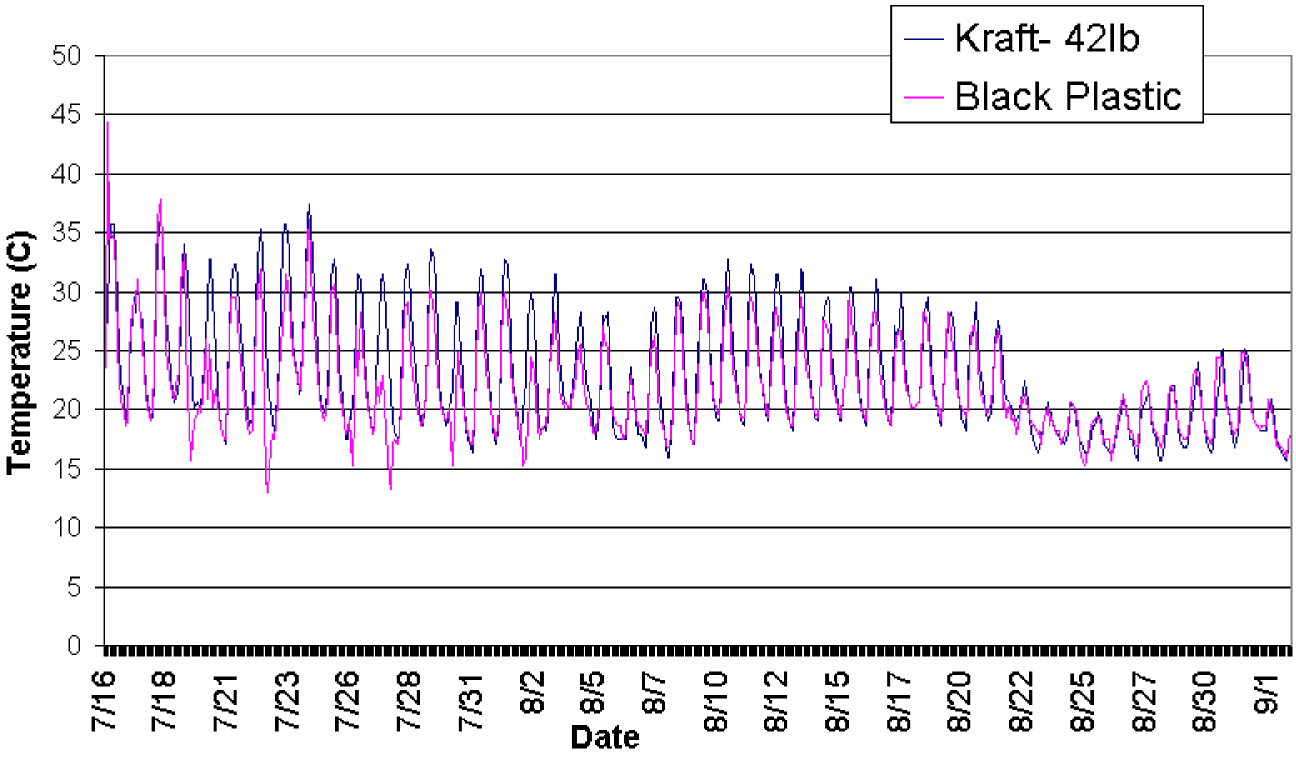


Figure 5: Garden Bio-Film and Black Plastic

Figure 6: Kraft-42 paper (plastic-coated) and Black Plastic



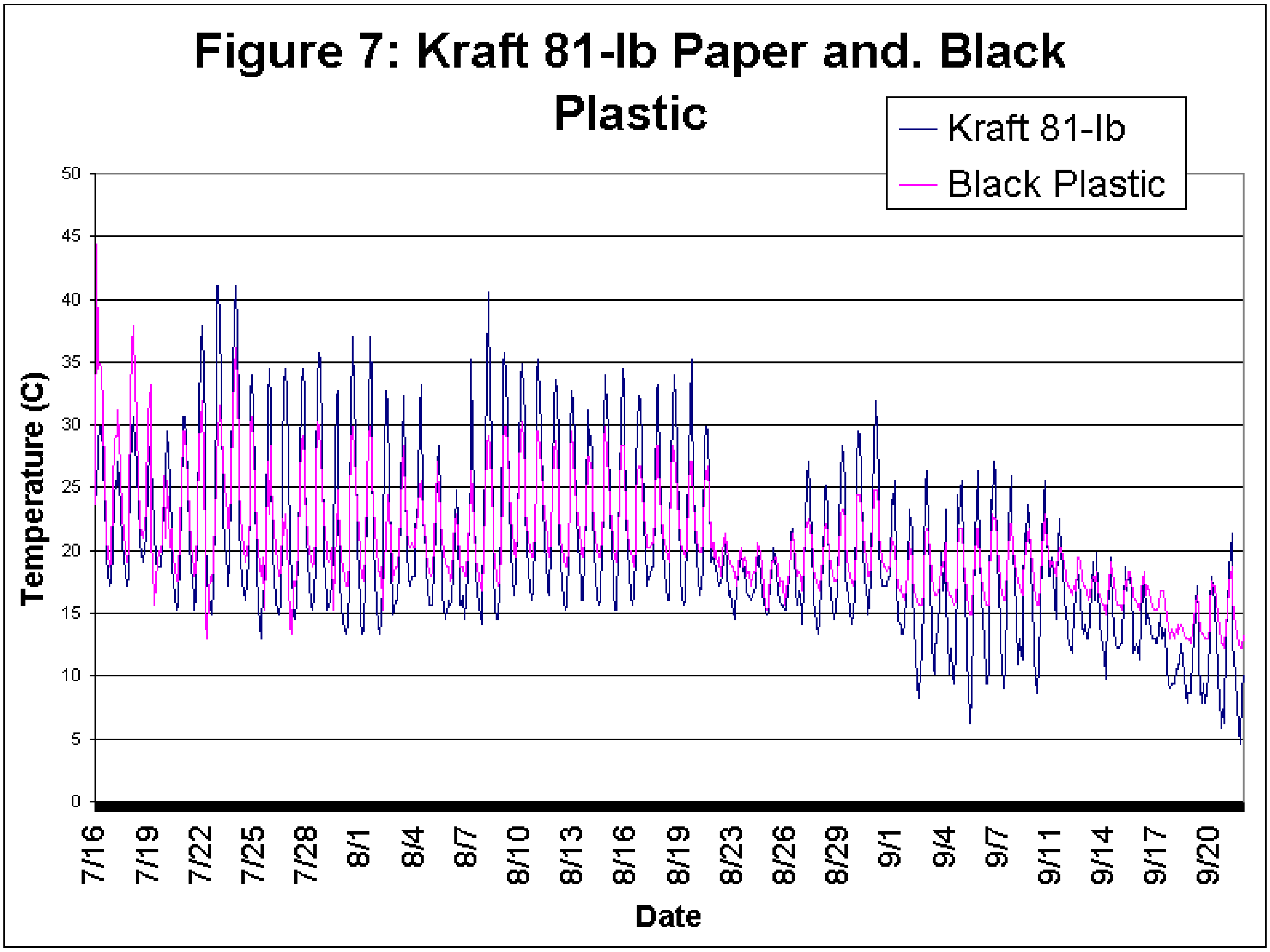


Figure 7: Kraft 81-lb Paper and. Black Plastic
Kraft 81-lb
Black Plastic
Temperature (C)
0
5
10
15
20
25
30
35
40
45
50
7/16
7/19
7/22
7/25
7/28
8/1
8/4
8/7
8/10
8/13
8/16
8/19
8/23
8/26
8/29
9/1
9/4
9/7
9/11
9/14
9/17
9/20
Date

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Introduction

Weed control is one of the primary concerns in organic farming as it is labor intensive, expensive and time consuming. Since its introduction in the 1950s, plastic mulch has become a standard practice used by many farmers to control weeds, increase crop yield, and shorten time to harvest (Lamont, 1991). Plastic mulch has contributed significantly to the economic viability of farmers worldwide, and by 1999 almost 30 million acres worldwide were covered with plastic mulch, with more than 185,000 of those acres in the United States (American Plastics Council, 2004; Takakura and Fang, 2001). However, each year farmers must dispose of their plastic, and although agricultural plastic recycling has begun, the disposal option that most choose is the landfill (Garthe, 2002). Many organic farmers, especially those who are small-scale, choose not to use plastic mulch because of the waste disposal issues. An effective, affordable, degradable alternative to the now-standard plastic mulch would contribute the same production benefits as plastic mulch and in addition would reduce non-recyclable waste.

Previous work. In 2003, we conducted a preliminary study at Washington State University Vancouver Research and Extension Unit (WSU VREU) to evaluate paper and cornstarch mulches as alternatives to plastic mulch. We used 81 lb Kraft paper with and without oil application. We evaluated three oils (soybean, linseed and tung) applied before and after laying the paper. ARS chemist Randal L. Shogren (2000) at the National Center for Agricultural Utilization Research found that Kraft paper treated with a combination of epoxidized soybean oil and citric acid was effective for 13 weeks in the field and withstood wind and rain better than untreated Kraft paper. A field evaluation by R. C. Hochmuth (2001) of the University of Florida found that watermelon grown on paper mulch coated with polymerized vegetable oil yielded on par with black plastic mulch. In our study at WSU VREU, the 81 lb Kraft paper mulch with and without oil proved as high in quality as the plastic mulch (Miles *et al.*, 2003). To follow up on these promising preliminary results, we conducted further studies in 2004 and 2005 to test different quality papers, additional mulch products and a diversity of vegetable crops.

Objectives

The purpose of this study is to identify and test degradable mulch products that can be used as effective and affordable alternatives to standard plastic mulch. We tested degradable mulches with four different vegetable crops in an organic production system to evaluate mulch durability and effects on soil temperature and crop yields. Different vegetable crops have different temperature needs, and it is possible each crop may perform best with a different mulch product.

Materials and Methods

We evaluated 5 alternative mulches in 2004 and 8 in 2005 (Table 1). Two of the products included both years were degradable plastic mulch that contain TDPA™ (Billingham, 2005). The 2 paper products that were tested in 2004 were eliminated because they were not suitable for organic systems. Five new paper products were added in 2005. Both years, mulch products were compared to black plastic (control) and were evaluated for durability, and effects on soil temperature and crop yield. In 2004, this study was conducted on a certified organic field, and in 2005 it was conducted on a non-certified field that was managed organically. Some of the products tested are not currently allowed in certified organic systems, and research such as this study is needed to determine their suitability.

Table 1. Descriptions of mulch products evaluated in 2004 and 2005 at WSU Vancouver REU.

Product	Description	Year Tested
42 lb Coated Kraft Paper	Brown paper coated with transparent polyethylene	2004
81 lb Kraft Paper	Brown paper bonded with cement	2004
Garden Biofilm	Cornstarch-based black film; 100% degradable	2004 & 2005
Envirocare 1	Black plastic w/ Ciba Envirocare TDPA (Totally Degradable Plastic Additive); 75 days to degredation	2004 & 2005
Envirocare 2	Black plastic w/ Ciba Envirocare TDPA (Totally Degradable Plastic Additive); 140 days to degredation	2004 & 2005
Black plastic (control)	1.0 mil embossed black polyethylene plastic film	2004 & 2005
Longview Fibre Paper (LF) 1	Raisin Tray Paper - highly sized, high wet strength; 15% recycled fiber	2005
LF 2	Leaf Bag Paper - normally sized, high wet strength; 28% recycled fiber	2005
LF 3	Raisin Tray Paper - highly sized, no wet strength; 12% recycled fiber	2005
LF 4	Bag Paper - normally sized, no wet strength; 40% recycled fiber	2005
Planters Paper	Kraft paper with black pigment; 100% recycled fiber	2005

The experimental design both years was a randomized complete block with four replications. Main plots were 55 feet long by 3 feet wide and each included 4 subplots, one for each of 4 vegetable crops. Vegetable crops were selected to represent 2 growing periods (short vs long) and 2 temperature regimes (cool vs warm): lettuce – short growing season, cool temperature; broccoli – long growing season, cool temperature; bell pepper – short growing season, warm temperature; and icebox watermelon – long growing season, warm temperature. It is important to note that all these crops are summer crops, two of them are simply short season (short) and two of them are heat loving (warm). Plants were seeded in the greenhouse mid-April both years, and transplanted into the field June 24 2004, and June 8 2005. “Pirat” lettuce, “Gypsy” broccoli, and “California Wonder” bell peppers were planted in double 10-foot-long rows, while “Smile” icebox watermelon was planted in a single 21-foot long row. Spacing in the row was 12 inches for lettuce (20 plants per plot), 20 inches for broccoli and peppers (12 plants per plot), and 3 feet for watermelon (7 plants per plot). Mulches were laid using a mulch layer tractor attachment, except for the Garden Biofilm, which was laid by hand. Drip tape was laid at the same time as the mulch, and plots were drip irrigated. After laying the mulches, holes were manually punched for each plant using a bulb setter. Vegetables were transplanted by hand, and were fertilized immediately after transplanting and every 3 weeks thereafter. Fertilizer was soluble BioLink (5-5-5) and soluble seaweed extract powder (Acadian 1-0-4 w/ trace minerals) applied through the irrigation system at a rate of 5 lb/A and 3 lb/A, respectively. Using Hobo field temperature monitors, we measured temperatures beneath each mulch product at the soil surface and at a 2-inch depth. Temperatures under the mulch were compared to bare soil.

Mulch quality was rated weekly on a scale of 0 to 9 where 0 was 0-9% mulch cover and 9 was 90-100% cover. Vegetables in each plot were harvested when they reached peak maturity, and yield measurements included total yield, marketable (trimmed) yield, number of marketable fruits/heads, and number of days to harvest. In 2004, black plastic and the paper coated with polyethylene were removed from the field following the final harvest and all other products were tilled into the soil. In 2005, black plastic was again removed from the field following the final harvest and all degradable products were tilled into the soil. However, only 2 plots each of the 2 Envirocare products were tilled and 2 plots were removed and were composted in separate on-farm compost piles.

Results and Discussion

Mulch products evaluated in this study showed significant differences in quality (durability) over time in both 2004 and 2005 (Figures 1 and 2). Black plastic was the most durable, with quality declining only slightly over the course of the growing season both years. Quality of Envirocare 2 and Envirocare 1 mulches was comparable to black plastic throughout both growing seasons. In 2004, Kraft 81-lb and Kraft 43-lb paper mulches exhibited fair quality at the end of the season, but were significantly less durable than black plastic and Envirocare mulches. However, both these paper products are unsuitable for organic systems and so they were not included in this study in 2005. The Kraft 81-lb was laminated with cement, a prohibited substance for organic farming, and the Kraft 43-lb polyethylene coated paper was extremely difficult to remove at the end of the season. In 2005, the 5 paper mulch products declined in quality relatively quickly, and were rated 5 or below (50% cover or less) only 5-6 weeks after field application. Weed growth occurred under all the paper mulches and was the major cause of their decline in quality. Weeds grew large enough to push the paper mulches off the ground, causing them to tear and eventually blow away. Weed growth under the paper mulch indicates there was significant light penetration through these products. Oil application to these paper mulch products may reduce light penetration and may be worth evaluation. Garden BioFilm was the least durable mulch in 2004, steadily declining to a final quality rating of 2 (20-29% cover), indicating that it was nearly gone at the end of the growing season. In 2005, Garden BioFilm quality dropped below 50% after 7 weeks in the field, and it’s quality rating remained slightly better than the paper mulches until 12 weeks after application, at which point it dropped below a rating of 2.

In 2004, different mulch products significantly affected broccoli and watermelon yields, but not yields of lettuce and pepper. In 2005, yields of all crops were significantly affected by mulch products, and yields in all paper plots were significantly lower due to their general degradation and the subsequent weed growth in those plots. Yield of lettuce was least impacted by mulch product due to its short time to harvest, and paper or cornstarch products may be most suitable for similar short season crops (Table 2). Envirocare 1 and 2 and Garden BioFilm resulted in the highest overall yield of lettuce both years. In general, there was very little variability in number of heads produced by the different mulch products.

Black plastic mulch resulted in high broccoli yield both years while Envirocare 1 and Envirocare 2 produced the lowest yields in 2004 and were high yielding in 2005 (Table 3). Paper products in 2005 resulted in the lowest broccoli yields. There was no significant difference in average broccoli head weight in 2004, but in 2005, all paper products resulted in lower head weight.

There were no significant differences in pepper yield in 2004, however in 2005, all paper products resulted in significantly lower yields (Table 4). Only average fruit weight of peppers due to LF3 was equivalent to plastic. Watermelon yield and number of fruit were significantly greater due to Envirocare 1 and Envirocare 2 both years (Table 5). Paper products resulted in significantly lower watermelon yields and fruit number than all other mulch treatments both years. Yield differences were primarily due to the number of fruit harvested.

Mulch quality was significantly correlated to crop yield in 2005 and as quality of mulch declined, yield declined (Table 6). Weed growth under the paper mulch products was the primary cause of their ripping which caused them to decline in quality. Weeds pushed up the mulches, causing them to rip along the edges where they were buried in the soil. Garden Biofilm began to degrade in longitudinal rips and weeds then grew in the exposed areas of the beds.

Harvest of all crops was 10-20 days later in 2005 than in 2004, due to cooler temperatures throughout the summer. In 2004, days to maturity from transplanting of broccoli was significantly affected by mulch product, and in 2005, broccoli and pepper were significantly affected (Table 7). In 2004, broccoli was harvested earliest from plots treated with Garden BioFilm, and latest from plots treated with black plastic. In 2005, broccoli was harvested earliest from Envirocare 1 and 2 plots and latest from paper plots except LF4, which was comparable to black plastic. Pepper was harvested earliest from black plastic plots and latest from paper plots except LF 3, which was comparable to black plastic.

In 2004, black plastic mulch showed an insulating effect on underlying soil. That is, minimum and maximum temperature beneath the mulch were less extreme than above it (Figure 3). Temperatures under all of the mulch products appeared similar to black plastic in their insulating effect, except for Kraft 81-lb paper, which showed greater extremes of both high and low temperatures. In 2005, maximum and minimum temperatures under all products differed significantly from black plastic. Minimum temperatures under LF1, LF2, LF3, LF4, and Planters Paper were lower than under black plastic. Maximum temperatures under LF1 and Planters Paper were greater than under black plastic. Maximum temperatures under Envirocare 1, Envirocare 2 and Garden Biofilm were less than black plastic, while minimum temperature under Envirocare 1 was higher, under Envirocare 2 was lower, and under Garden Biofilm was the same as under black plastic.

Approximate costs per acre were calculated for 80% mulch cover. Black plastic costs $252 - $281 per acre, and may differ depending on the source. Envirocare films are similar in price to black plastic, ranging from $215 to $243 per acre, and the cost of Garden Bio-Film is higher, ranging from $695 to $1087. The cost of the LF paper products can vary over the year and the relatively heavy weight of paper makes shipping costs higher for paper mulches.

Both years, degradable mulch products were tilled into the soil following the final harvest, and by the following spring, the paper and cornstarch products had completely degraded while the 2 Envirocare products had not. In 2005, in addition to plowing down 2 plots each of both Envirocare products, we also removed both products from 2 plots each prior to plow-down and added the products to 2 separate on-farm compost piles (feedstock: fresh horse manure with bedding). We monitored temperatures in both compost piles throughout the winter/spring

(Figures 12 and 13) and by April 28 found that both Envirocare products had not degraded in this composting environment.

Conclusions

Envirocare 1 and Envirocare 2 are as durable as black plastic in the field and result in similar crop yield. However, in this study results indicate that Envirocare products did not degrade when they were incorporated into the field or when they were incorporated into on-farm compost piles. Garden Biofilm degrades completely in the soil, but it does not retain its quality long enough to be useful for long season crops. LF and Planters Paper products were suitable for a short season crop such as lettuce, but did not retain their quality for a long season crop such as watermelon. Once mulch cover fell below 50% (a quality rating of 5 or below), the product was ineffective for weed control or temperature modification. The extensive weed growth under all the paper mulch products indicates there was significant light penetration through these products.

The Kraft 81-lb and Kraft 43-lb paper mulches that were tested in 2004 were unsuitable for organic systems because the first was laminated with cement, a prohibited substance in organic farming, and the polyethylene coating on the second made it extremely difficult to remove (and removal is required by organic standards).

We plan to repeat this trial in 2006, using reformulated paper LF products and new additional cornstarch biofilms.

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Garthe, J. W. 2002. Used agricultural plastic mulch as a supplemental boiler fuel. An Overview of Combustion Test Results for Public Dissemination. Energy Institute, Penn State. <http://environmentalrisk.cornell.edu/C&ER/PlasticsDisposal/AgPlasticsRecycling/References/Garthe2002b.pdf>

Hochmuth, R.C. 2001. Field evaluation of watermelon produced on paper mulch coated with polymerized vegetable oil. North Florida Research and Education Center. Suwanee Valley, FL. <http://nfrec-sv.ifas.ufl.edu/reports_mulch.htm>

Lamont, W. J. 1991. The use of plastic mulches for vegetable production. Food and Fertilizer Technology Center. Kansas State University, Manhattan. <www.agnet.org/library/article/eb333.html>

Miles, C., Lydia Garth, Madhu Sonde, and Martin Nicholson. 2003. Searching for alternatives to plastic mulch. <http://agsyst.wsu.edu/MulchReport03.pdf>

Shogren, R.L. 2000. Biodegradable mulches from renewable resources. Journal of Sustainable Agriculture. 16:33-47.

Takakura, T., and W. Fang. 2001. Climate under cover. Kluwer Academic Publishers p 1-10 <http://ecaaser3.ecaa.ntu.edu.tw/weifang/Bio-ctrl/cuc-chap1.pdf>

Mulch Sources:

LF Paper products 1-4: Longview Fibre Company; 300 Fibre Way, P. O. Box 639, Longview, WA 98632; (360) 425-1550; www.longviewfibre.com

Planters Paper: Ken-Bar, Inc.; 25 Walkers Brook Drive, Reading, MA 01867-0704; 781-944-0003; www.ken-bar.com

Envirocare 1 and 2: Pliant Corporation; 1475 Woodfield Road, Suite 700, Schaumberg, IL, 60173; 866-878-6188; www.pliantcorp.com

Garden Bio-Film: BIOgroupUSA, Inc., 107 Regents PI., Ponte Vedra Beach, FL 32082; 904-280-5094; www.biogroupusa.com

Kraft 81-lb Paper: Newark Paperboard Products; 620 11th Ave., Longview, WA, 98632; 360-423-3420; www.newarkgroup.com (*No longer available from this source)*

Kraft 42-lb Polyethylene-coated Paper: Graphic Packaging; 814 Livingston Court, Marietta, GA, 30067; 770-644-3000; www.graphicpkg.com

Black plastic: Peaceful Valley Farm Supply P.O. Box 2209, Grass Valley, CA 95945; (530) 272-4769; www.groworganic.com

Seed Sources:

Lettuce: Variety: Pirat, from Wild Garden Seed www.wildgardenseed.com

Broccoli: 2004 Varieties: Gypsy and Green Goliath from Burpee, www.burpee.com
2005 Variety: Gypsy, from Sakata, distributed by Snow Seed Organic; www.snowseedco.com/organic.html

Watermelon: Variety: Smile, from America Takii Seeds, www.takii.com

Peppers: Variety: California Wonder, from Terra Organics; www.terraorganics.com

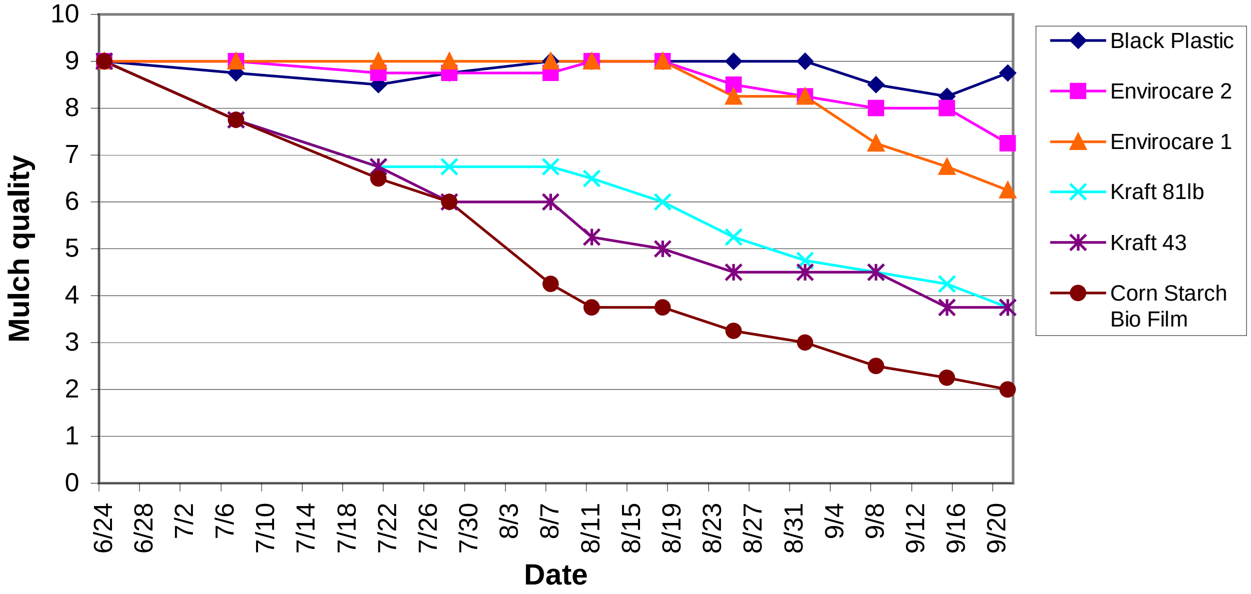

Figure 1: Mulch durability (quality over time) on a scale 0-9, where 0 is 0-9% mulch cover and 9 is 90-100% cover, in 2004 at WSU Vancouver REU.

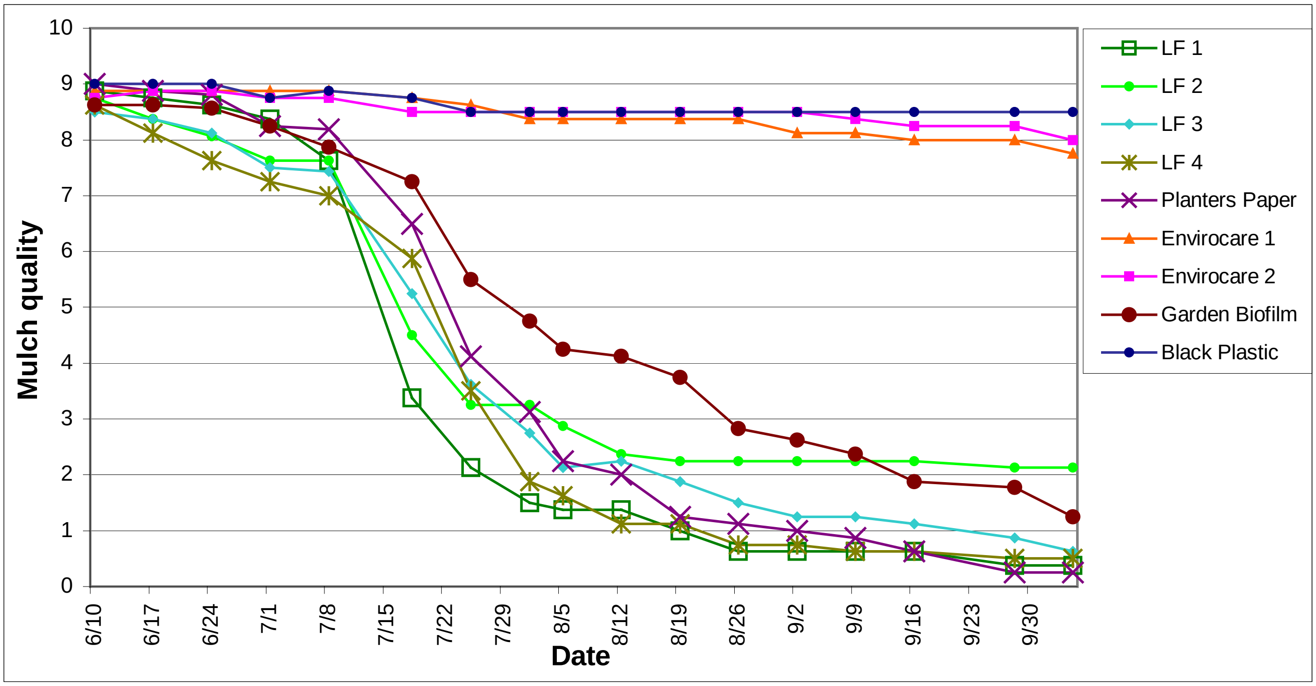

Figure 2. Mulch durability (quality over time) on a scale 0-9, where 0 is 0-9% mulch cover and 9 is 90-100% cover, in 2005 at WSU Vancouver REU.

Table 2. Mean marketable yield (kg) of lettuce, number of marketable heads per plot, and weight per head (g) in 2004 and 2005.

Mulch Product	Yield (kg)		No. Heads		Head Wt. (g)	
	2004	2005	2004	2005	2004	2005
Black plastic	4.98 a	4.77 abc	18 a	19 a	276 a	202 abc
Envirocare 1	6.05 a	5.06 ab	20 a	19 a	306 a	211 ab
Envirocare 2	4.63 a	5.58 a	18 a	18 a	251 a	259 a
Garden BioFilm	5.03 a	5.55 a	20 a	19 a	252 a	245 a
Kraft 42	4.91 a		20 a		246 a	
Kraft 81lb	4.47 a		19 a		232 a	
LF 1		1.11 e		6 b		92 e
LF 2		3.04 d		20 a		127 de
LF 3		3.36 cd		17 a		141 cde
LF 4		3.83 bcd		18 a		180 bcd
Planters Paper		3.71 bcd		19 a		155 bcde
P Value	**0.4588**	**0.0000**	**0.5945**	**0.0000**	**0.2225**	**0.0006**

Table 3. Mean marketable yield (kg) of broccoli, number of marketable heads per plot, and weight per head (g) in 2004 and 2005.

Mulch	Yield (kg)		No. Heads		Head Wt. (g)	
	2004	2005	2004	2005	2004	2005
Black plastic	7.28 a	3.08 abc	12.8 a	11.0 ab	655 a	280 ab
Envirocare 1	4.01 b	4.19 a	6.8 b	11.5 ab	651 a	370 a
Envirocare 2	3.22 b	3.96 ab	5.3 b	11.0 ab	573 a	360 a
Garden BioFilm	4.78 ab	2.98 bc	6.3 b	11.0 ab	762 a	270 ab
Kraft 42	3.95 b		6.0 b		641 a	
Kraft 81lb	4.68 ab		7.0 b		684 a	
LF 1		1.57 d		9.8 b		150 c
LF 2		2.29 cd		11.8 ab		190 bc
LF 3		2.18 cd		9.8 b		210 bc
LF 4		2.59 cd		11.3 ab		230 bc
Planters Paper		2.03 cd		12.0 a		170 c
P Value	**0.1046**	**0.0061**	**0.0910**	**0.5566**	**0.8605**	**0.0008**

Table 4. Mean marketable yield (kg) of pepper, number of marketable fruit per plot, and weight per fruit (g) in 2004 and 2005.

	Yield (kg)		**No. Fruit**		**Fruit Wt. (g)**	
Mulch	**2004**	**2005**	**2004**	**2005**	**2004**	**2005**
Black plastic	19.48 a	3.56 a	79 a	38.75 b	253 a	90 a
Envirocare 1	14.60 a	4.76 a	82 a	56.75 a	178 a	90 a
Envirocare 2	13.44 a	3.89 a	77.3 a	45.75 ab	175 a	80 a
Garden BioFilm	22.11 a	3.68 a	80.5 a	41.5 ab	270 a	90 a
Kraft 42	15.90 a		62.8 a		227 a	
Kraft 81lb	11.23 a		70.5 a		164 a	
LF 1		0.2 b		5.25 c		40 d
LF 2		0.51 b		9.5 c		60 bc
LF 3		0.68 b		8.5 c		80 ab
LF 4		0.15 b		3.75 c		30 d
Planters Paper		0.06 b		1.25 c		50 cd
P Value	**0.6797**	**0.0000**	**0.5653**	**0.0000**	**0.7115**	**0.0000**

Table 5. Mean marketable yield (kg) of watermelon, number of marketable fruit per plot, and weight per fruit (g) in 2004 and 2005.

	Yield (kg)		**No. Fruit**		**Fruit Wt. (kg)**	
Mulch	**2004**	**2005**	**2004**	**2005**	**2004**	**2005**
Black plastic	55.1 a	16.2 c	18.8 ab	9.0 c	3.1 a	1.8 b
Envirocare 1	71.2 a	37.7 a	24.0 a	15.5 a	2.9 a	2.4 a
Envirocare 2	50.4 ab	26.9 b	17.5 ab	10.8 bc	2.8 a	2.4 a
Garden BioFilm	47.5 ab	20.0 bc	16.3 abc	12.5 ab	3.0 a	1.5 bc
Kraft 42	44.9 ab		13.8 bc		3.2 a	
Kraft 81lb	19.6 b		7.0 c		2.7 a	
LF 1		1.0 d		1.3 d		0.6 d
LF 2		4.4 d		4.5 d		1.1 cd
LF 3		0.6 d		1.3 d		0.5 d
LF 4		3.0 d		3.5 d		0.8 d
Planters Paper		2.0 d		2.3 d		0.8 d
P Value	**0.0650**	**0.0000**	**0.0307**	**0.0000**	**0.5727**	**0.0000**

Table 6. Correlation between mulch quality and yield in 2005.

Correlation of mean mulch quality and total yield		
	r-value	p-value
Broccoli	0.8733	0.0021
Peppers	0.8907	0.0013
Watermelons	0.8594	0.0030
Lettuce		

Correlation of final mulch quality and total yield		
	r-value	p-value
Broccoli	0.835	0.0051
Peppers	0.8253	0.0062
Watermelons	0.804	0.009
Lettuce		

Table 7. Days after transplanting to maturity of lettuce, broccoli, pepper and watermelon in 2004 and 2005.

	Lettuce		Broccoli		Pepper		Watermelon	
Mulch	**2004**	**2005**	**2004**	**2005**	**2004**	**2005**	**2004**	**2005**
Black plastic	34	46	76	84 cd	91	102 d	85	106 ab
Envirocare 1	33	46	67	80d	89	106bcd	80	103 ab
Envirocare 2	35	46	71	80 d	89	109 bc	83	104 ab
Garden BioFilm	34	46	67	85bcd	85	105cd	83	96 b
Kraft 42	34		68		87		83	
Kraft 81lb	33		68		86		88	
LF 1		46		97 a		115 a		115 a
LF 2		46		91ab		111ab		105 ab
LF 3		46		97 a		106 bcd		103 ab
LF 4		46		88bc		114a		106 ab
Planters Paper		46		91 ab		117 a		111 a
P Value	**0.5875**	**n/a**	**0.0687**	**0.0001**	**0.3536**	**0.0002**	**0.5414**	**0.3405**

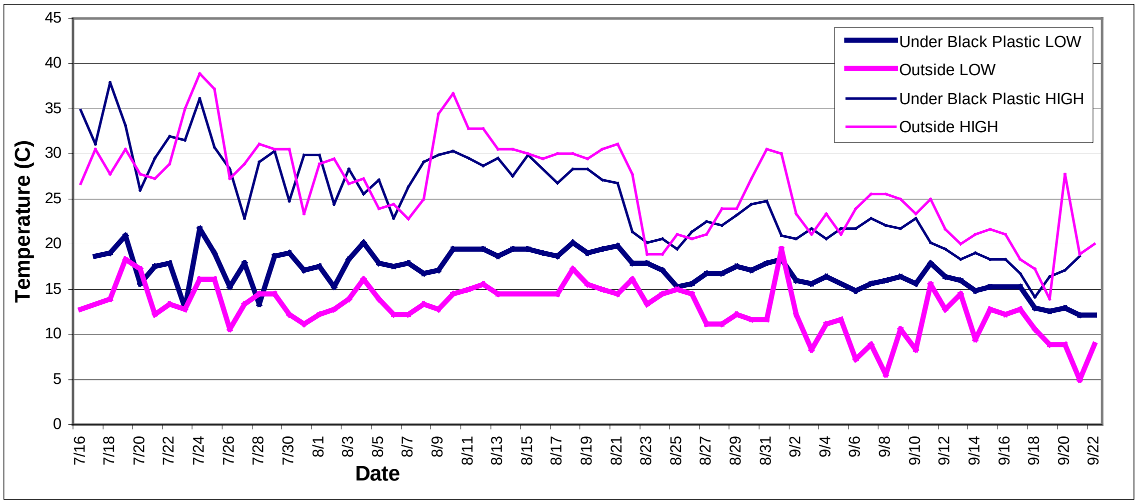

Figure 3. Maximum and minimum temperatures under black plastic and at the soil surface on bare ground in 2004.

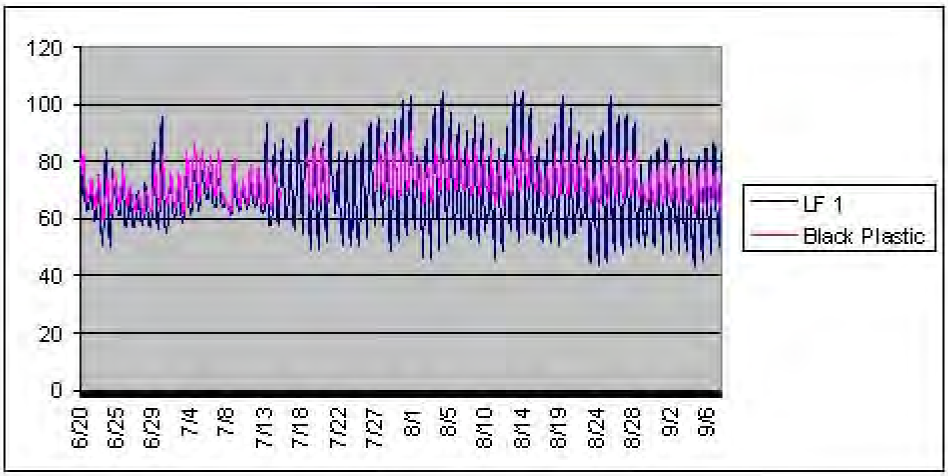

Figure 4. Temperatures under black plastic and under LF 1 paper mulch in 2005.

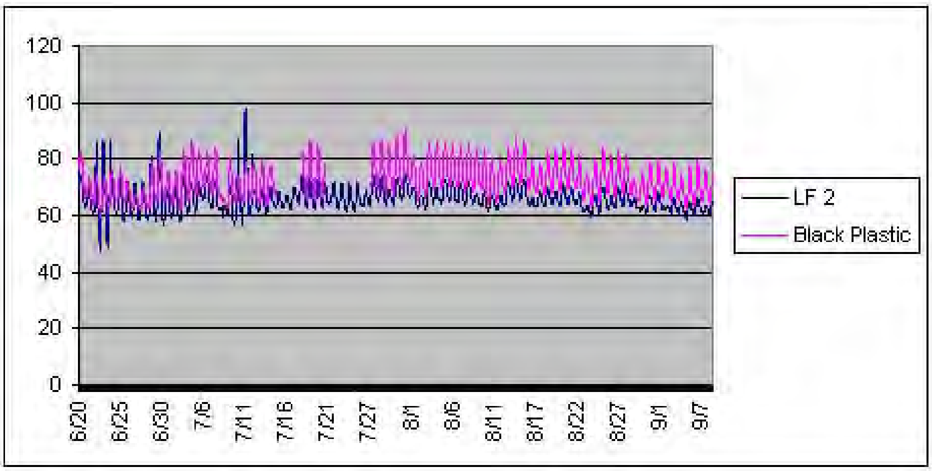

Figure 5. Temperatures under black plastic and under LF 2 paper mulch in 2005.

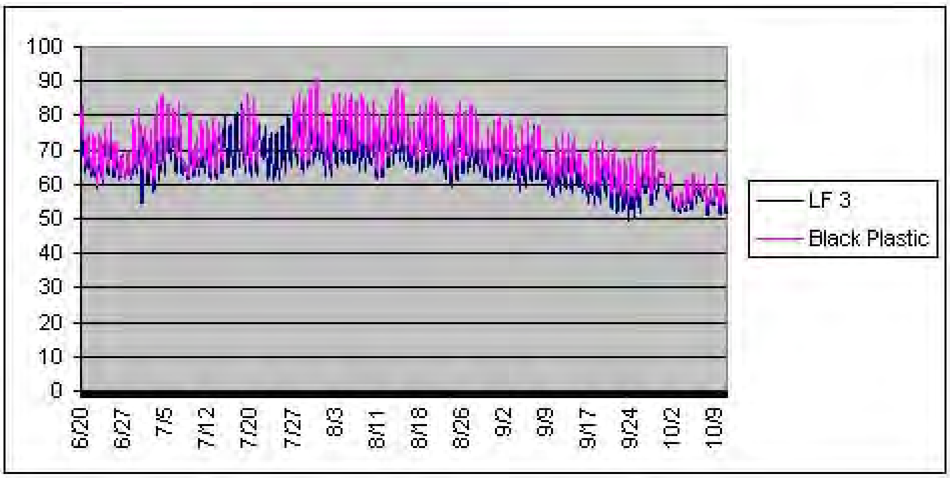

Figure 6. Temperatures under black plastic and under LF 3 paper mulch in 2005.

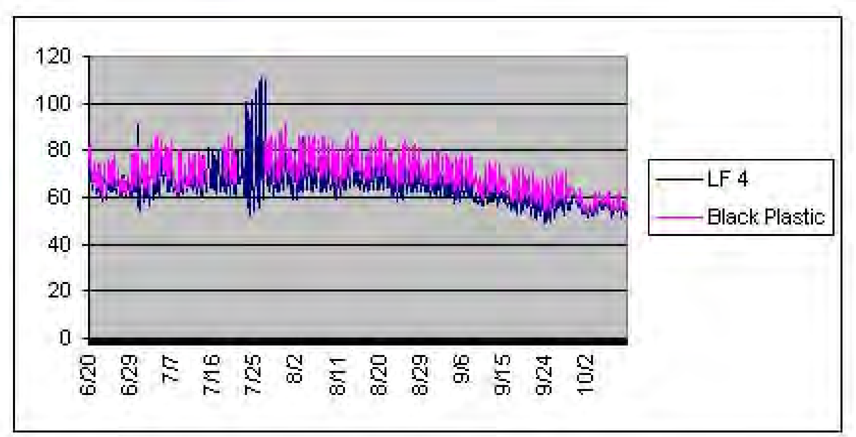

Figure 7. Temperatures under black plastic and under LF 4 paper mulch in 2005.

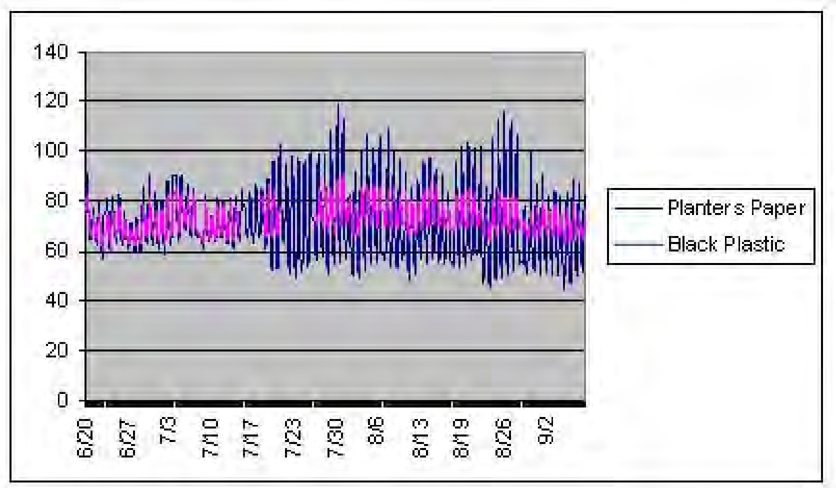

Figure 8. Temperatures under black plastic and under Planters Paper mulch in 2005.

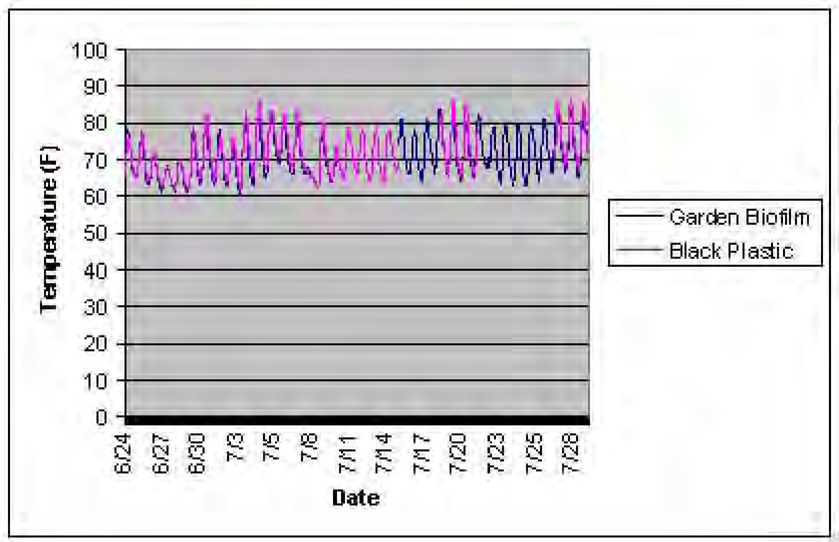

Figure 9. Temperatures under black plastic and under Garden Biofilm mulch in 2005.

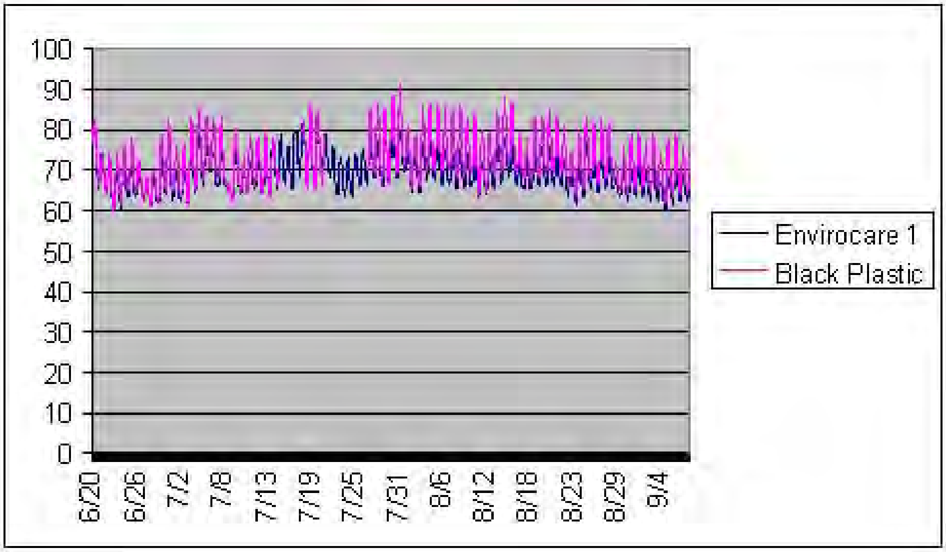

Figure 10. Temperatures under black plastic and under Envirocare 1 mulch in 2005.

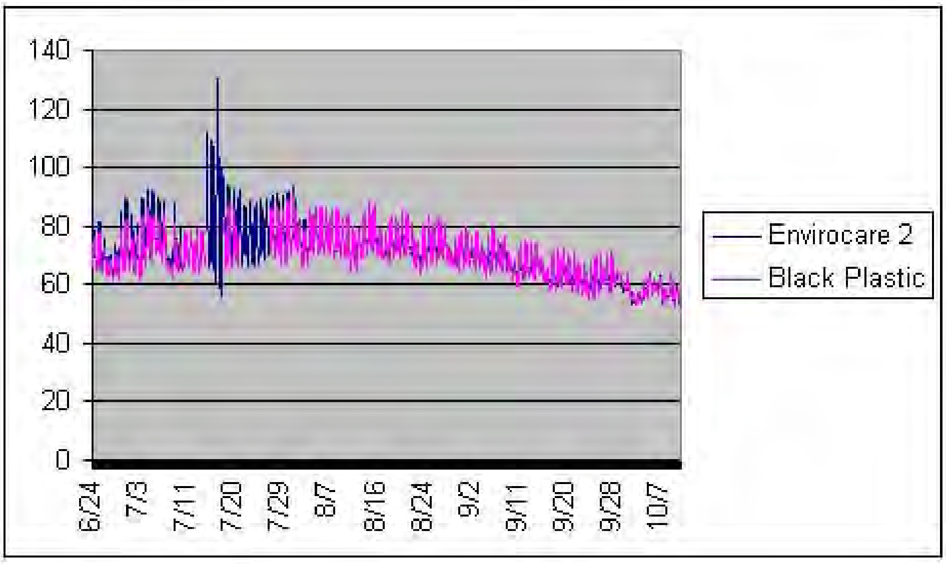

Figure 11. Temperatures under black plastic and under Envirocare 2 mulch in 2005.

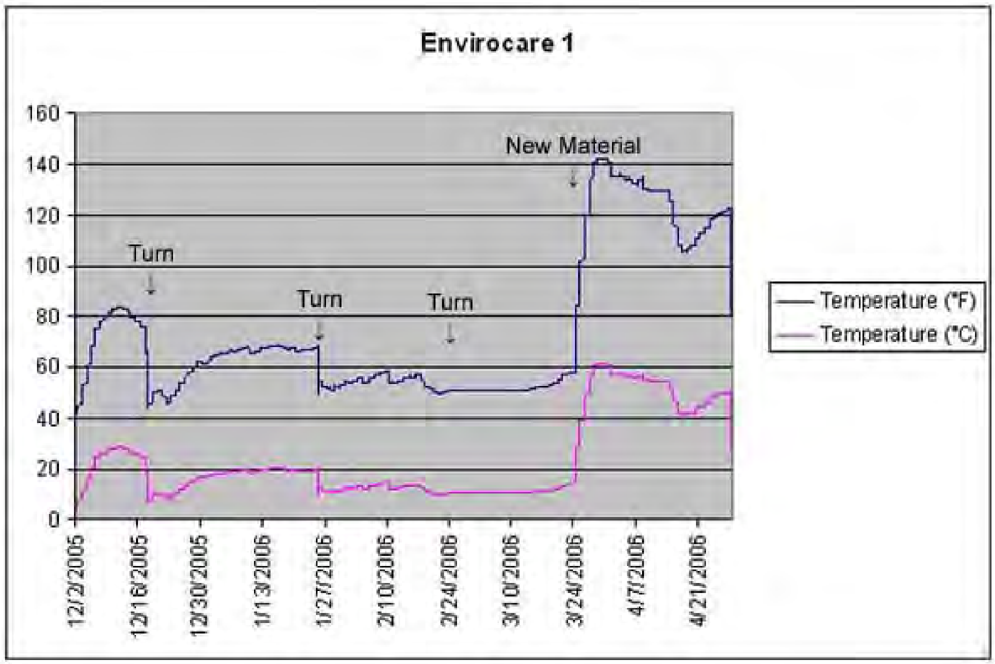

Figure 12. Temperatures in on-farm compost pile from December through April that included Envirocare 1 mulch product.

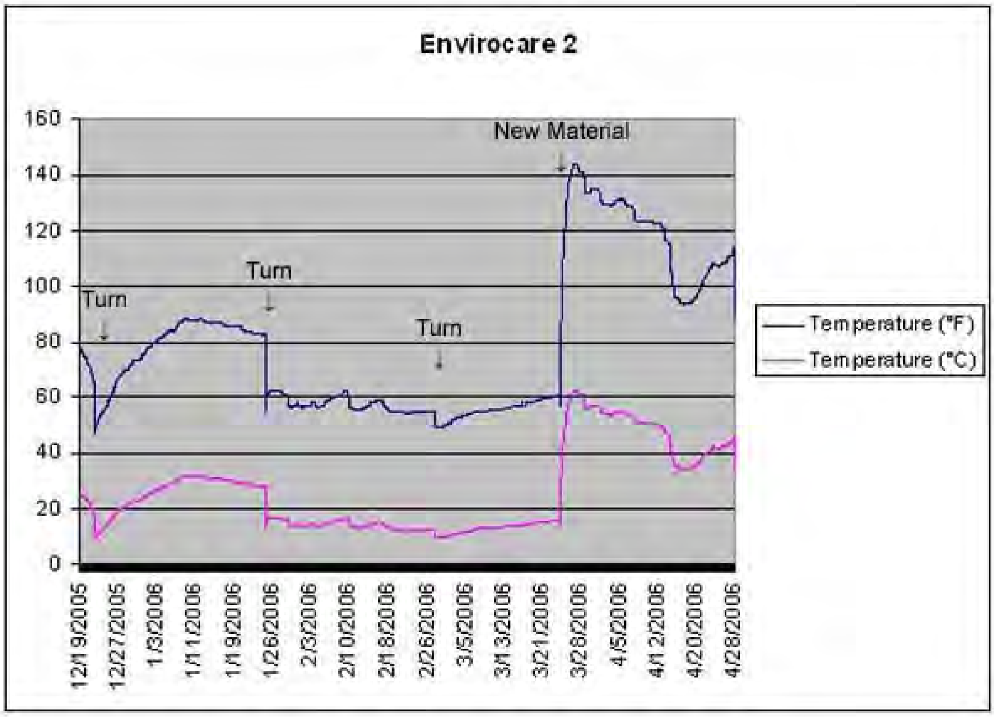

Figure 13. Temperatures in on-farm compost pile from December through April that included Envirocare 2 mulch product.

Alternatives to Plastic Mulch in Vegetable Production Systems

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Introduction

Since its introduction in the 1950s, plastic mulch has become a standard practice used by many farmers to control weeds, increase crop yield, and shorten time to harvest (Lamont, 1991). Plastic mulch has contributed significantly to the economic viability of farmers worldwide, and by 2006 it was estimated that 400,000 acres were covered with plastic mulch in the United States (American Plastics Council, 2004; Takakura and Fang, 2001; Bergholtz, 2006). Due to tracking difficulties it is currently impossible to determine the true number of acres in the U.S. (Garthe, 2006). Each year farmers must dispose of their plastic and the disposal option that most choose is the landfill (Garthe, 2002). Many small-scale and organic farmers choose not to use plastic mulch because of the waste disposal issues. Ideally, farmers would like to plow down the mulch at the end of the season, thereby eliminating removal as well as disposal costs (Sorkin, 2006). Degradable plastics were introduced in the 1980's; however, there remains many questions regarding their efficacy, degradability and potential residues (Vert *et al*., 1992; Riggle, 1998; Shogren, 2000; Hockmuth, 2001). For organic farming, degradable mulches would need to meet National Organic Program (NOP) standards.

The purpose of this study was to identify and test degradable mulch products that can be used as effective and affordable alternatives to standard plastic mulch (Miles, *et.al*., 2005) We tested degradable mulches with four different vegetable crops in an organic vegetable production system to evaluate mulch durability and effects on soil temperature and crop yields. Different vegetable crops have different temperature needs, and it is possible each crop may perform best with a different mulch product.

Materials and Methods

We evaluated 8 alternative mulches in a field study in 2005 and 10 in 2006 (Table 1). This study was conducted on a field that was managed organically but was not certified organic. Some of the products tested may not currently be allowed in organic systems, and research such as this study is needed to determine their suitability.

The experimental design both years was a randomized complete block with four replications. Main plots were 55 feet long by 3 feet wide and each included 4 subplots, one for each of 4 vegetable crops. Vegetable crops were selected to represent 2 growing periods (short vs. long) and 2 temperature regimes (cool vs. warm): lettuce – short growing season, cool temperature; broccoli – long growing season, cool temperature; bell pepper – short growing season, warm temperature; and icebox watermelon – long growing season, warm temperature. Plants were seeded in the greenhouse mid-April both years, and transplanted into the field June 8, 2005 and June 9, 2006. "Pirat" lettuce, "Gypsy" broccoli, and "California Wonder" bell peppers were planted in double 10-foot-long rows, while "Smile" icebox watermelon was planted in a single 21-foot long row. Spacing in the row was 12 inches for lettuce (20 plants per plot), 20 inches for broccoli and peppers (12 plants per plot), and 3 feet for watermelon (7 plants per plot) (Figure 1).

Mulches were laid using a mulch layer tractor attachment, except for the Garden Biofilm in 2005, which was laid by hand. Drip tape was laid at the same time as the mulch. After laying the mulches, holes were manually punched using a bulb setter and vegetables were transplanted by hand. Plots were drip irrigated once a week at the rate of 1 inch. Plants were fertigated immediately after transplanting and every 3 weeks thereafter. Fertilizer was soluble BioLink (5-5-5) and soluble seaweed extract powder (Acadian 1-0-4 w/ trace minerals) applied at a rate of 5 lb/A and 3 lb/A, respectively. Temperatures were measured with Hobo field monitors beneath each mulch product at the soil surface and at a 2-inch depth in the neighboring bare soil.

Table 1. Descriptions of mulch products evaluated in 2005 and 2006 at Washington State University Vancouver REU. This table is not intended to be used to promote any products listed or detract from any products not included in this field study.

Product	Description	Year Tested
Black plastic (control)	1.0 mil embossed black polyethylene plastic film	2005, 2006
Envirocare 1	Black plastic w/ Ciba Envirocare TDPA (Totally Degradable Plastic Additive); 75 days to degradation	2005, 2006
Envirocare 2	Black plastic w/ Ciba Envirocare TDPA (Totally Degradable Plastic Additive); 140 days to degradation	2005, 2006
Garden Biofilm	Cornstarch-based black film, 100% degradable;	2005, 2006
Garden Biofilm NF01U/P 15 mic	Cornstarch-based black film, 100% degradable; developed for short cycle crops	2006
Garden Biofilm NF803/P 12 mic	Cornstarch-based black film, 100% degradable; developed for longer cycle crops	2006
Garden Biofilm NF803/P 15 mic	Cornstarch-based black film, 100% degradable; developed for longer cycle crops	2006
Planters Paper	Kraft paper with black pigment; 100% recycled fiber	2005, 2006
Longview Fibre Paper (LF) 1	Raisin Tray Paper - highly sized, high wet strength; 15% recycled fiber	2005
LF 2	Leaf Bag Paper - normally sized, high wet strength; 28% recycled fiber	2005
LF 3	Raisin Tray Paper - highly sized, no wet strength; 12% recycled fiber	2005
LF 4	Bag Paper - normally sized, no wet strength; 40% recycled fiber	2005, 2006
LF 5	Hi STFI Liner (Hi Performance Liner) - medium sized, medium wet strength, 18% recycled fiber	2006

Mulch quality was rated weekly on a scale of 0 to 9 where 0 was 0-9% mulch cover and 9 was 90-100% cover. Vegetables in each plot were harvested when they reached peak maturity, and yield measurements included marketable yield, number of marketable fruits/heads, and number of days to first harvest. In 2005, black plastic was removed from the field following the final harvest and all products except Envirocare 1 and Envirocare 2 were incorporated into the soil using a rototiller/rotovator. Two plots of each Envirocare 1 and Envirocare 2 were rototilled into the soil while 2 plots were removed and composted in separate on-farm compost piles. In 2006, Envirocare 1 and Envirocare 2 were removed from the field at the same time as black plastic and all other products were tilled into the soil.

Figure 1. Field trial of alternatives to plastic mulch at WSU Vancouver REU in 2006.

Results and Discussion

Mulch products evaluated in this study showed significant differences in quality (durability) over time (Figure 2). In 2005, black plastic, Envirocare 2 and Envirocare 1 were the most durable, with quality declining only slightly over the course of the growing season. The 5 paper mulch products declined in quality relatively quickly, and were rated 5 or below (50% cover or less) only 5-6 weeks after field application. Weed growth occurred under all the paper mulches, indicating there was significant light penetration, and was the major cause of their decline in quality. Weeds grew large enough to push the paper mulches off the ground, causing the mulches to rip along the edges where they were buried in the soil, and eventually blow away. Garden BioFilm quality dropped below 50% after 7 weeks in the field, and it's quality rating remained slightly better than the paper mulches until 12 weeks after application, at which point it dropped below a rating of 2. Garden Biofilm began to degrade in longitudinal rips and weeds then grew in the exposed areas of the beds.

In 2006, black plastic, Envirocare 1, Envirocare 2 and LF 5 were the most durable products, with quality declining by less than 20% over the course of the growing season. Paper mulch LF 4 declined in quality in a similar fashion as in 2005 while Planters Paper was considerably more durable in 2006 than in 2005, indicating a significant variation in performance. In 2006 just as in 2005, weed growth occurred under the LF 4 paper mulch, and this was the primary cause of its decline in quality. The 4 cornstarch mulch products varied from each other in quality over the season, with Garden Biofilm NF01U/P15 being the most durable followed by Garden Biofilm NF803/P15. Garden Biofilm declined in quality in 2006 in a similar fashion as in 2005.

Yields differed significantly between years and were lower for all crops in 2006 than in 2005. Both years, yields with paper mulches tended to be lower than with other mulch products, and these differences were significant for some crops. In general, yield of lettuce and broccoli (both cool season crops) were least impacted by paper mulch whereas yield of pepper and watermelon (both warm season crops) were more greatly impacted. In 2005, all paper mulches exhibited a general degradation early in the season and weeds subsequently grew throughout those plots, resulting in low yields. In 2006, only LF 4 degraded early and yields were consequently lower than for other products.

In 2005, Envirocare 1 and 2 and Garden Biofilm resulted in the highest overall yield of lettuce but there was little variability in the number of lettuce heads (Table 2). Black plastic mulch resulted in high broccoli yield, followed closely by Envirocare 1 and Envirocare 2. Paper products resulted in the lowest broccoli yields. All paper products resulted in significantly lower pepper yields while only LF3 resulted in mean fruit weight equivalent to plastic (Table 3). Watermelon yield and number of fruit were significantly greater due to Envirocare 1 and Envirocare 2, and paper products resulted in significantly lower watermelon yields and fruit number than all other mulch treatments. Watermelon yield differences were primarily due to the number of fruit harvested.

In 2006, lettuce yield and number of heads tended to be greatest with Envirocare 2, LF 5, and Garden Biofilm NF803/12 and lowest with black plastic, Garden Biofilm, and LF 4, however these differences were not significant (Table 2). Broccoli yield tended to be greatest with Garden Biofilm NF803/15, Envirocare 2, and Garden Biofilm NF803/12, and lowest with LF 5, Planters Paper and black plastic, however these differences were not significant (Table 3). Numbers of broccoli heads were greatest with Envirocare 2 and Garden Biofilm, and lowest with Garden Biofilm NF01U/P15. The average head weight of broccoli was greatest with Garden Biofilm NF803/15 and Garden Biofilm NF803/12, and lowest with black plastic and Garden Biofilm. Pepper yield and number of fruit were greatest with Garden Biofilm NF803/15, Envirocare 2 and Envirocare 1, and lowest with LF 4, Planters Paper and black plastic (Table 4). Watermelon yield and fruit number were greatest with Envirocare 1, Envirocare 2 and Garden Biofilm NF803/15, and lowest with LF 4 and LF 5 (Table 5). The average fruit weight of watermelon was greatest with Envirocare 1 and Envirocare 2, and lowest with LF 5.

Mulch products had a significant effect on days to maturity for all crops both in 2005 or 2006, however these effects were generally not consistent (Table 6). However, Envirocare 1 and Envirocare 2 resulted in earlier yields of broccoli both years and of watermelon in 2006.

Both years, maximum and minimum temperatures under all products differed significantly from black plastic (Figures 3-10). Minimum temperatures under LF1, LF2, LF4, and Planters Paper were lower than under black plastic, and minimum temperatures under LF3 and LF5 were the same as under black plastic. Maximum temperatures under LF1 and Planters Paper were greater, under LF2 and LF3 were lower, and under LF4 and LF5 were the same as under black plastic. Maximum temperatures under Envirocare 1 varied substantially by year, but minimum temperatures were the same as under black plastic both years. Maximum and minimum temperatures under Envirocare 2 were lower than under black plastic. Maximum and minimum temperatures under Garden Biofilm NF01U/P15, Garden Biofilm NF803/P12, and Garden Biofilm NF803/P15were the same as under black plastic.

In 2005, paper, cornstarch and 2 plots each of Envirocare 1 and Envirocare 2 mulch products were tilled into the soil in October following the final harvest. By spring 2006, the paper and cornstarch products had completely degraded in the field while Envirocare 1 and Envirocare 2 had not. Also in 2005, two plots each of Envirocare 1 and Envirocare 2 were added to two separate on-farm compost piles (feedstock: fresh horse manure with bedding). By April 28 2006, Envirocare 1 and Envirocare 2 had not degraded in on-farm composting. In 2006, Envirocare 1 and Envirocare 2 were removed from the field at the same time as black plastic and all other mulch products were tilled into the soil.

Conclusions

In this study, once mulch cover fell below 50% (a quality rating of 5 or below), the product was ineffective for weed control. The extensive weed growth under all the paper mulch products in 2005 was the primary reason for yield decline with those mulch products.

Envirocare 1 and Envirocare 2 were as durable as black plastic in the field and resulted in similar crop yield. Preliminary results indicate that LF 5 is almost as durable as black plastic however it may be more suitable for cool season crops and not as well suited for warm season crops. Temperatures under LF 5 were greater than or equal to temperatures under black plastic so it is not clear why crop yields tended to be lower. The new cornstarch product Garden Biofilm NF803/P15 appeared somewhat durable in the field and had the added benefit of resulting in higher crop yields than black plastic, likely due to the higher maximum temperatures that occurred under this mulch as compared to black plastic. Garden Biofilm NF01U/P15 was more durable in the field than Garden Biofilm NF803/P15 but did not result in greatly increased yields. Garden Biofilm and Garden Biofilm NF803/P12 did not retain their mulch quality beyond mid August, however yields were comparable to or better than with black plastic. Planters Paper had poor quality the first year and good quality the second year of this study, perhaps indicating variability in batch quality. In addition, yields of all crops with Planters Paper tended to be lower than for other mulch products.

In this study Envirocare products did not degrade when they were incorporated into the field or when they were incorporated into on-farm compost piles. Therefore these products did not provide reduced farm labor costs or disposal fees. Ideally, degradable mulch would degrade in the soil, eliminating the removal and disposal costs.

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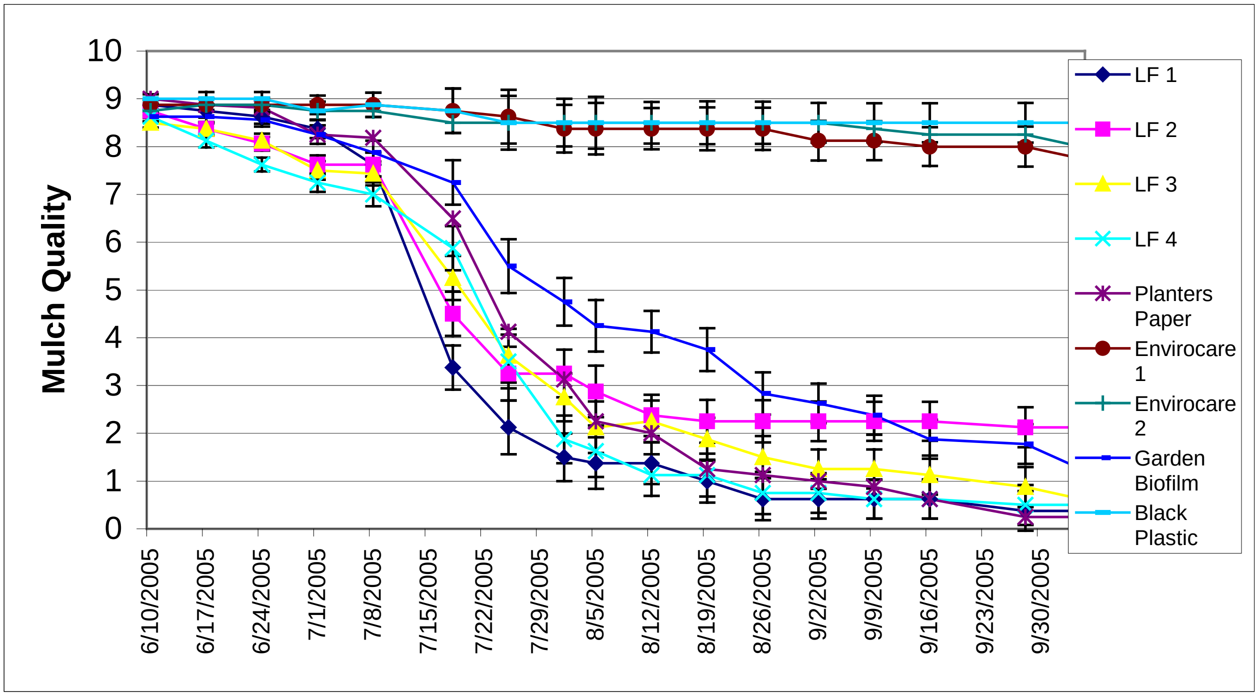


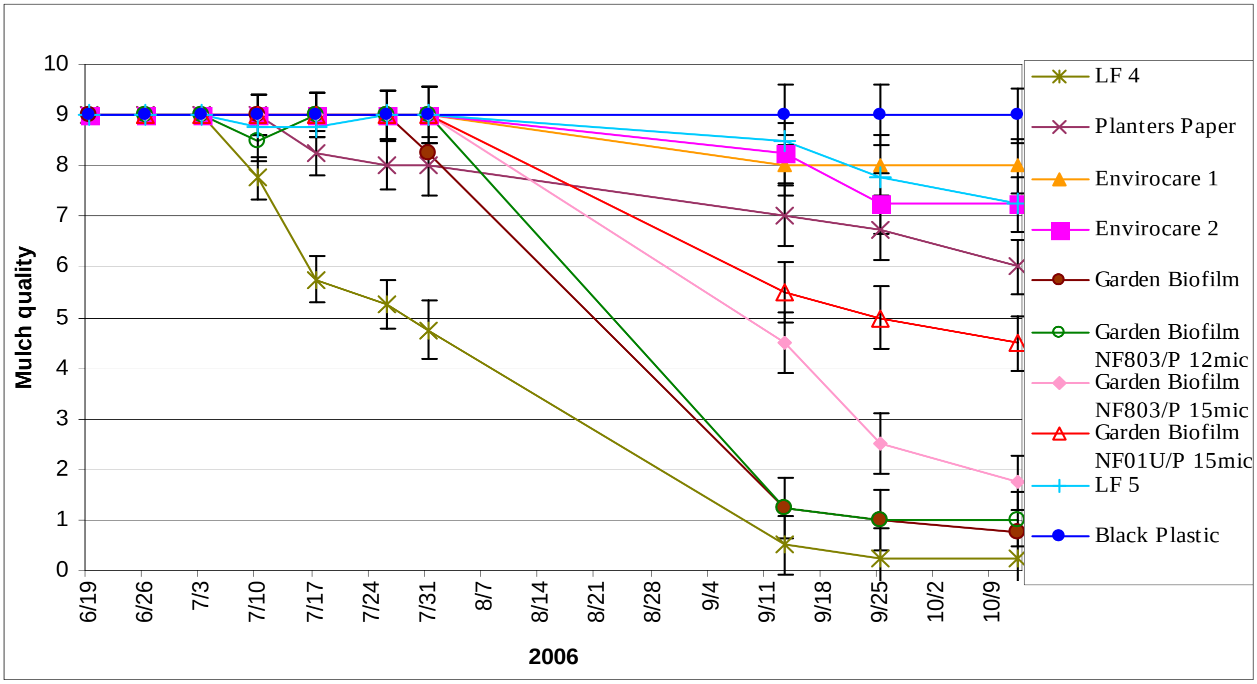


Figure 2. Mulch durability (quality over time) on a scale 0-9, where 0 is 0-9% mulch cover and 9 is 90-100% cover, in 2005 and 2006 at WSU Vancouver REU.

Table 2. Mean marketable yield (kg) of lettuce, number of marketable heads per plot, and weight per head (g) in 2005 and 2006.

	Yield (kg)		No. Heads		Head Wt. (g)	
Mulch Product	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**
Black plastic	4.77 abc	2.14 a	19 a	16 a	202 abc	135 a
Envirocare 1	5.06 ab	2.59 a	19 a	16 a	211 ab	162 a
Envirocare 2	5.58 a	2.86 a	18 a	17 a	259 a	171 a
LF 1	1.11 e		6 b		92 e	
LF 2	3.04 d		20 a		127 de	
LF 3	3.36 cd		17 a		141 cde	
LF 4	3.83 bcd	2.31 a	18 a	16 a	180 bcd	142 a
LF 5		2.73 a		17 a		162 a
Planters Paper	3.71 bcd	2.43 a	19 a	16 a	155 bcde	154 a
Garden Biofilm	5.55 a	2.20 a	19 a	20 a	245 a	125 a
Garden Biofilm NF803/12		2.62 a		17 a		154 a
Garden Biofilm NF01U/P15		2.33 a		18 a		131 a
Garden Biofilm NF803/15		2.33 a		16 a		144 a
P Value	**0.0000**	**0.6475**	**0.0000**	**0.8960**	**0.0006**	**0.2336**

Table 3. Mean marketable yield (kg) of broccoli, number of marketable heads per plot, and weight per head (g) in 2005 and 2006

	Yield (kg)		No. Heads		Head Wt. (g)	
Mulch	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**
Black plastic	3.08 abc	1.18 a	11.0 a	8.3 abc	280 ab	137 d
Envirocare 1	4.19 a	1.50 a	11.5 a	8.8 ab	370 a	164 cd
Envirocare 2	3.96 ab	1.78 a	11.0 a	9.8 a	360 a	183 bcd
LF 1	1.57 d		9.8 a		150 c	
LF 2	2.29 cd		11.8 a		190 bc	
LF 3	2.18 cd		9.8 a		210 bc	
LF 4	2.59 cd	1.25 a	11.3 a	7.8 abcd	230 bc	162 cd
LF 5		1.14 a		6.3 cd		188 bcd
Planters Paper	2.03 cd	1.15 a	12.0 a	7.8 abcd	170 c	150 cd
Garden Biofilm	2.98 bc	1.29 a	11.0 a	9.5 a	270 ab	137 d
Garden Biofilm NF803/12		1.66 a		6.5 bcd		258 ab
Garden Biofilm NF01U/P15		1.36 a		5.8 d		234 abc
Garden Biofilm NF803/15		2.03 a		6.5 bcd		318 a
P Value	**0.0061**	**0.2506**	**0.5566**	**0.0167**	**0.0008**	**0.0032**

Table 4. Mean marketable yield (kg) of pepper, number of marketable fruit per plot, and weight per fruit (g) in 2005 and 2006.

	Yield (kg)		No. Fruit		Fruit Wt. (g)	
Mulch	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**
Black plastic	3.56 a	1.86 abc	38.75 b	15.8 abc	90 a	114 a
Envirocare 1	4.76 a	3.31 ab	56.75 a	27.8 ab	90 a	118 a
Envirocare 2	3.89 a	3.70 ab	45.75 ab	29.5 ab	80 a	126 a
LF 1	0.2 b		5.25 c		40 d	
LF 2	0.51 b		9.5 c		60 bc	
LF 3	0.68 b		8.5 c		80 ab	
LF 4	0.15 b	0.40 c	3.75 c	3.8 c	30 d	107 a
LF 5		2.11 abc		19.0 abc		111 a
Planters Paper	0.06 b	1.51 bc	1.25 c	13.8 bc	50 cd	113 a
Garden Biofilm	3.68 a	2.67 abc	41.5 ab	21.0 abc	90 a	129 a
Garden Biofilm NF803/12		2.52 abc		18.8 abc		159 a
Garden Biofilm NF01U/P15		3.01 ab		27.8 ab		108 a
Garden Biofilm NF803/15		4.09 a		34.0 a		119 a
P Value	**0.0000**	**0.0002**	**0.0000**	**0.0003**	**0.0000**	**0.4957**

Table 5. Mean marketable yield (kg) of watermelon, number of marketable fruit per plot, and weight per fruit (g) in 2005 and 2006

	Yield (kg)		No. Fruit		Fruit Wt. (kg)	
Mulch	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**
Black plastic	16.2 c	11.4 ab	9 c	6.5 ab	1.8 b	1.7 ab
Envirocare 1	37.7 a	27.3 a	15.5 a	12.8 a	2.4 a	2.2 a
Envirocare 2	26.9 b	20.2 ab	10.8 bc	10.8 ab	2.4 a	2 ab
LF 1	1 d		1.3 d		0.6 d	
LF 2	4.4 d		4.5 d		1.1 cd	
LF 3	0.6 d		1.3 d		0.5 d	
LF 4	3 d	1.9 b	3.5 d	1.5 b	0.8 d	1.3 ab
LF 5		6.6 b		6.5 ab		1.1 b
Planters Paper	2 d	10.5 ab	2.3 d	6.8 ab	0.8 d	1.4 ab
Garden Biofilm	20 bc	14.6 ab	12.5 ab	8.3 ab	1.5 bc	1.8 ab
Garden Biofilm NF803/12		12.7 ab		8.5 ab		1.5 ab
Garden Biofilm NF01U/P15		18 ab		13.8 a		1.3 ab
Garden Biofilm NF803/15		18.7 ab		11 ab		1.7 ab
P Value	**0.0000**	**0.0023**	**0.0000**	**0.0077**	**0.0000**	**0.0471**

Table 6. Days after transplanting to first harvest of lettuce, broccoli, pepper and watermelon at WSU Vancouver REU in 2005 and 2006.

	Lettuce		Broccoli		Pepper		Watermelon	
Mulch	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**
Black plastic	46	39 a	84 cd	71 bc	102 d	109 a	106 ab	72 abcd
Envirocare 1	46	39 a	80 d	67 c	106 bcd	109 a	103 ab	65 d
Envirocare 2	46	39 a	80 d	67 c	109 bc	109 a	104 ab	67 cd
LF 1	46		97 a		115 a		115 a	
LF 2	46		91 ab		111 ab		105 ab	
LF 3	46		97 a		106 bcd		103 ab	
LF 4	46	40 a	88 bc	69 bc	114 a	113 a	106 ab	81 a
LF 5		38 a		70 bc		109 a		78 a
Planters Paper	46	39 a	91 ab	70 bc	117 a	109 a	111 a	69 bcd
Garden Biofilm	46	38 a	85 bcd	68 c	105 cd	109 a	96 b	65 d
Garden BiofilmNF803/12		34 b		74 bc		112 a		77 ab
Garden BiofilmNF01U/P15		35 b		84 a		109 a		68 cd
GardenBiofilmNF803/15		34 b		84 a		109 a		74 abcd
P Value	**n/a**	**0.0000**	**0.0001**	**0.0000**	**0.0002**	**0.124**	**0.3405**	**0.0100**

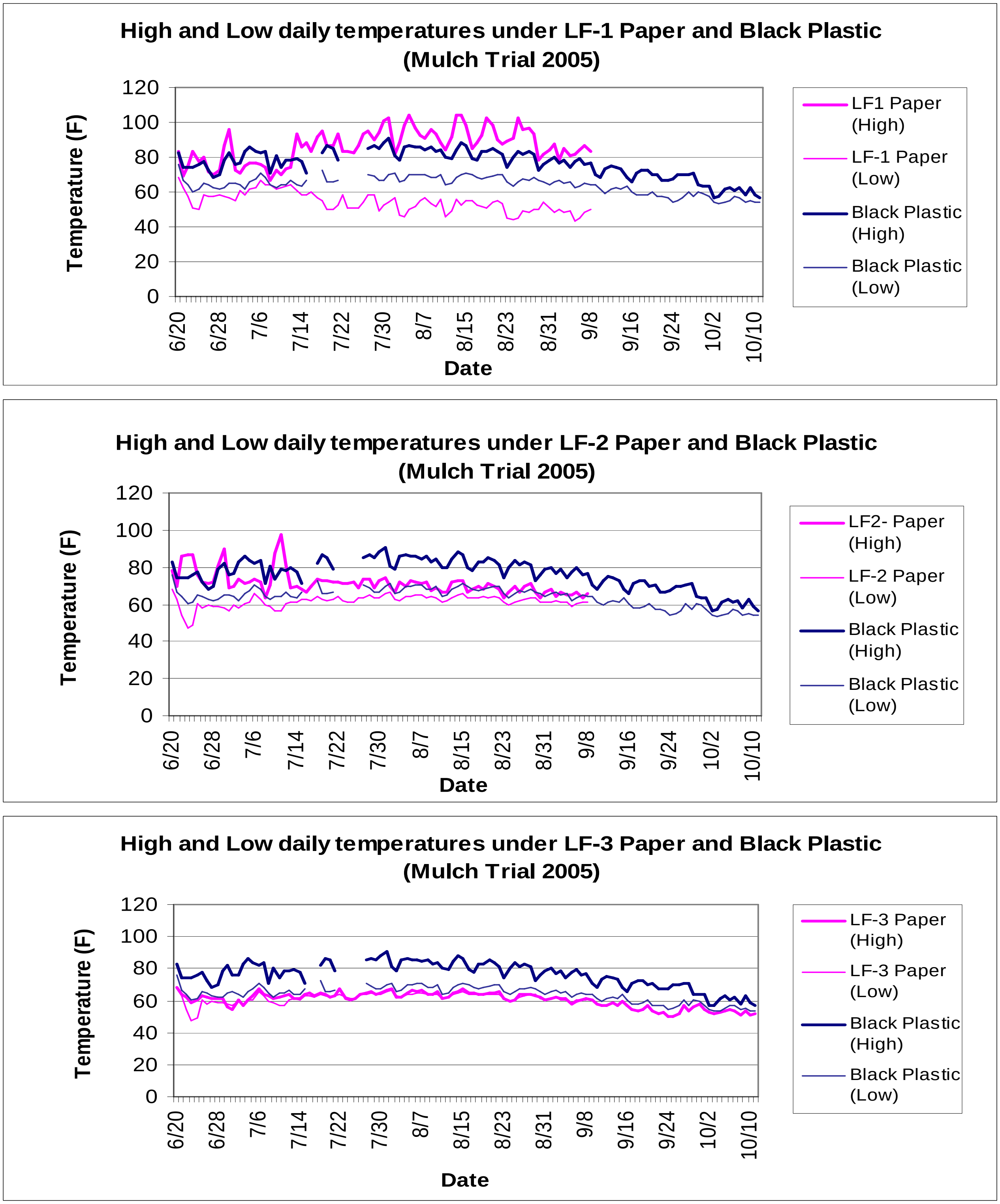
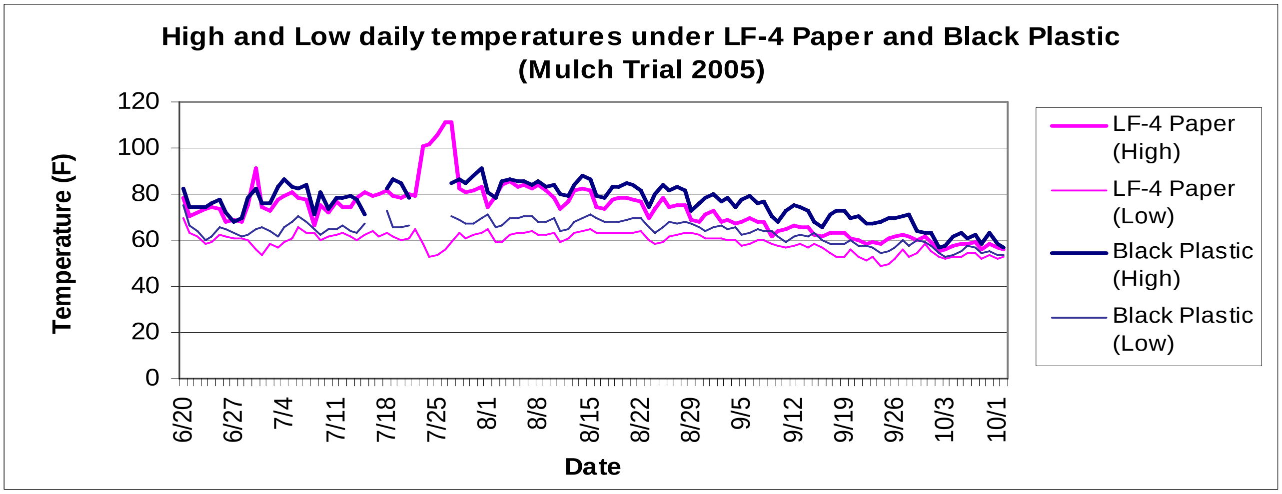


Figure 3. Temperatures (^{o}F) measured under black plastic and under LF 1, LF 2, and LF 3 paper mulches in 2005.



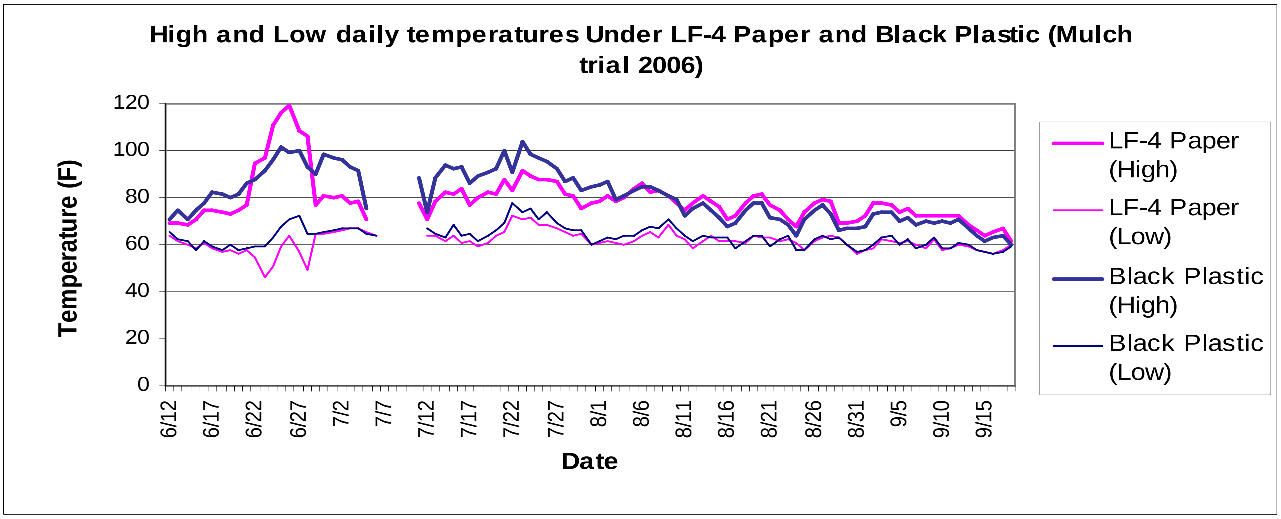


Figure 4. Temperatures (^{o}F) measured under black plastic and under LF 4 paper mulch in 2005 and 2006.

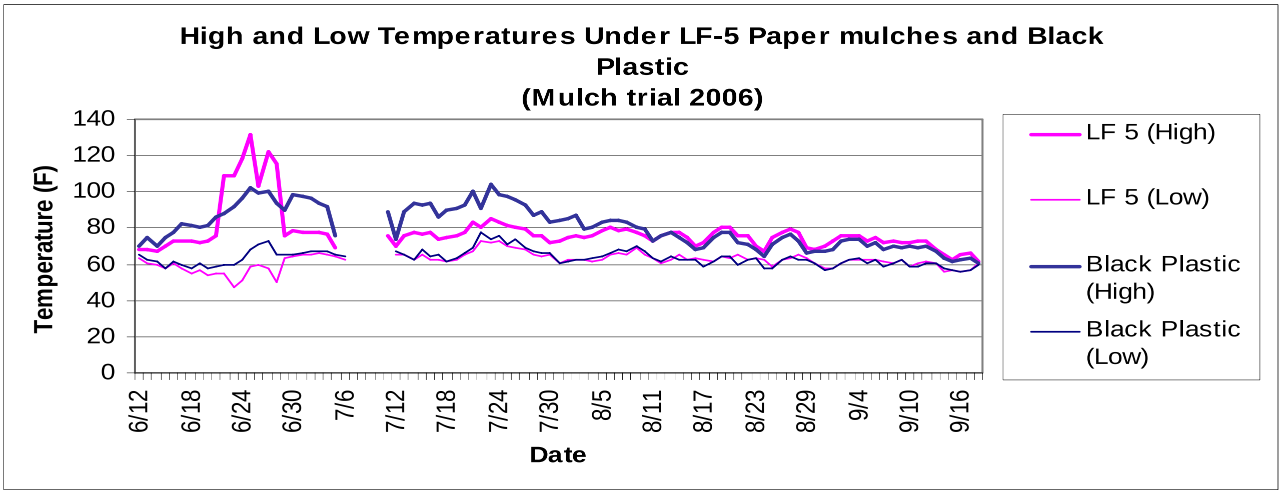
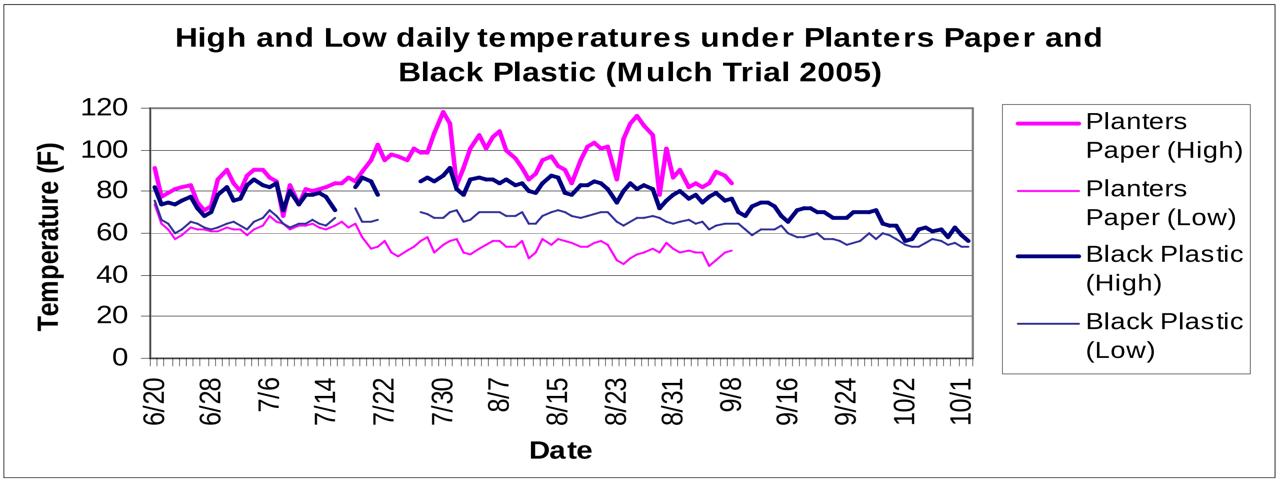


Figure 5. Temperatures (^{o}F) measured under black plastic and under LF 5 paper mulch in 2006.



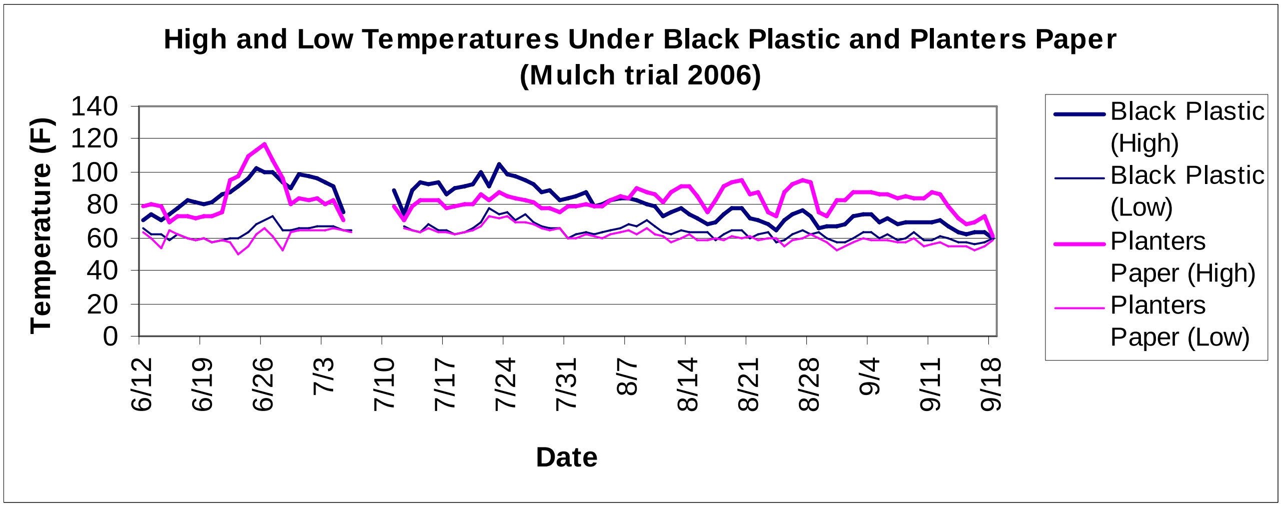
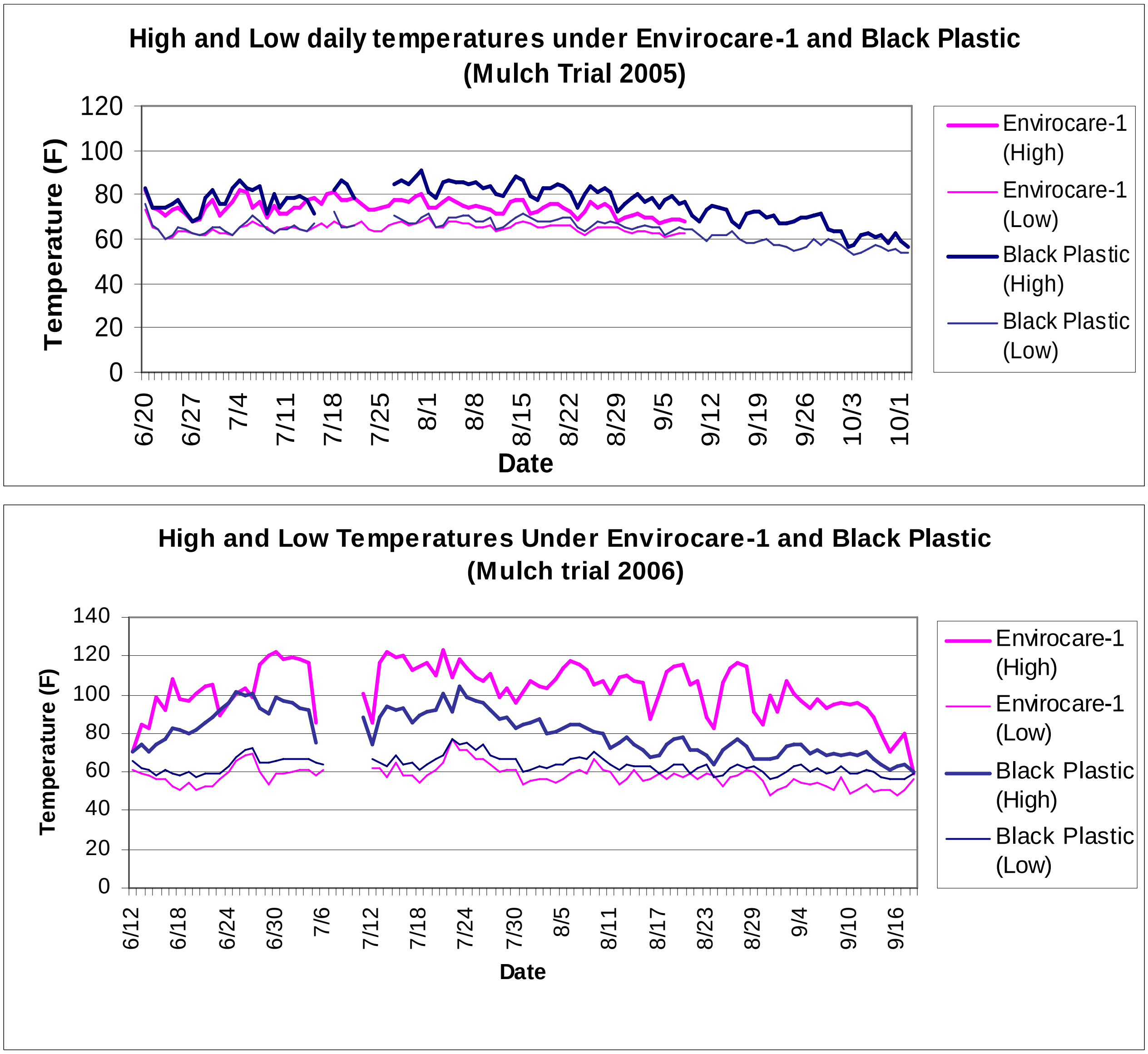
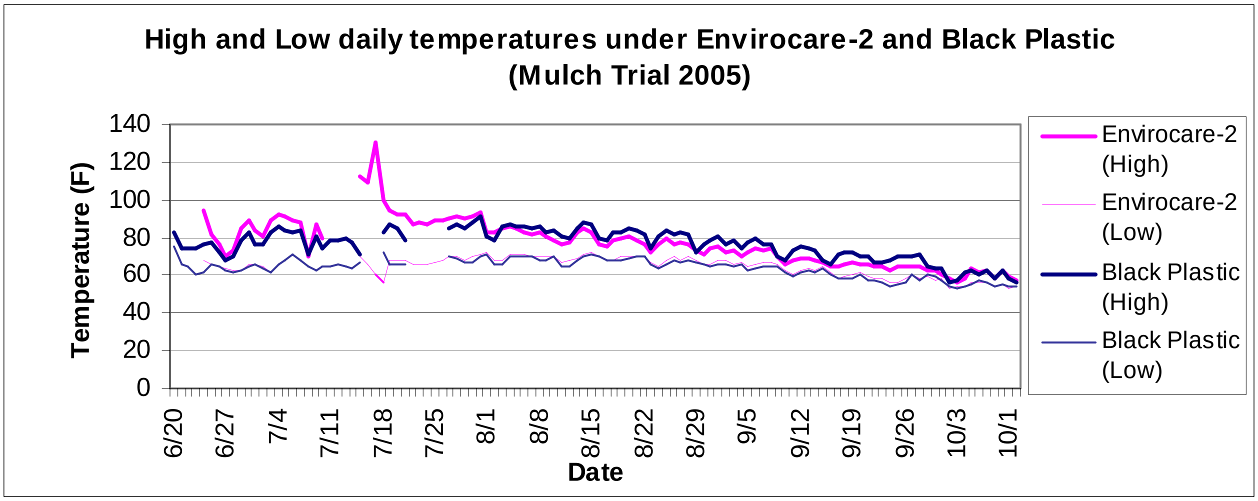


Figure 6. Temperatures (^{o}F) measured under black plastic and under Planters Paper mulch in 2005 and 2006.


High and Low daily temperatures under Envirocare-1 and Black Plastic (Mulch Trial 2005)

High and Low Temperatures Under Envirocare-1 and Black Plastic (Mulch trial 2006)

Figure 7. Temperatures (^{o}F) measured under black plastic and under Envirocare 1 mulch in 2005 and 2006.



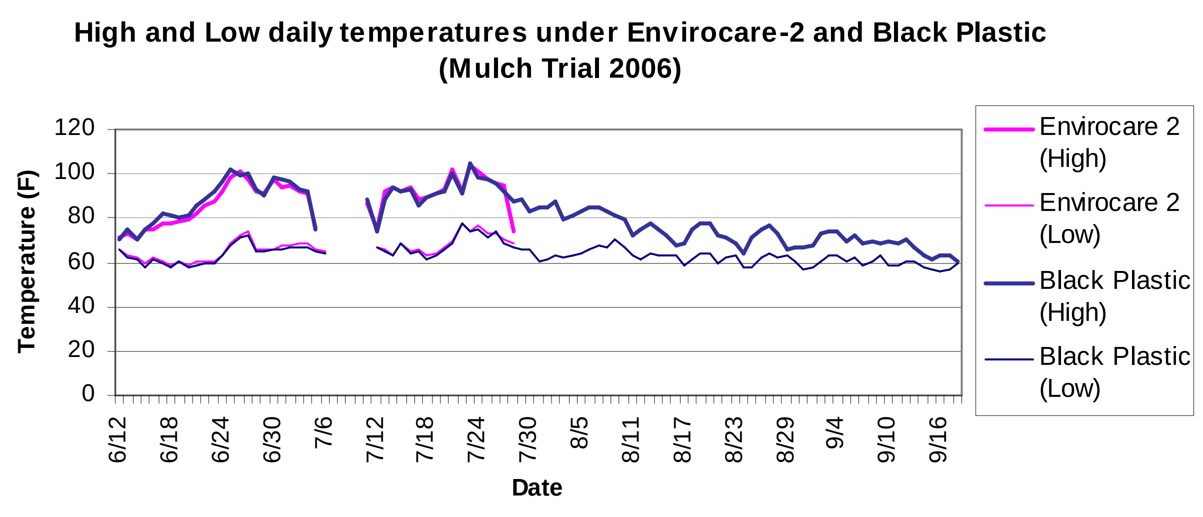
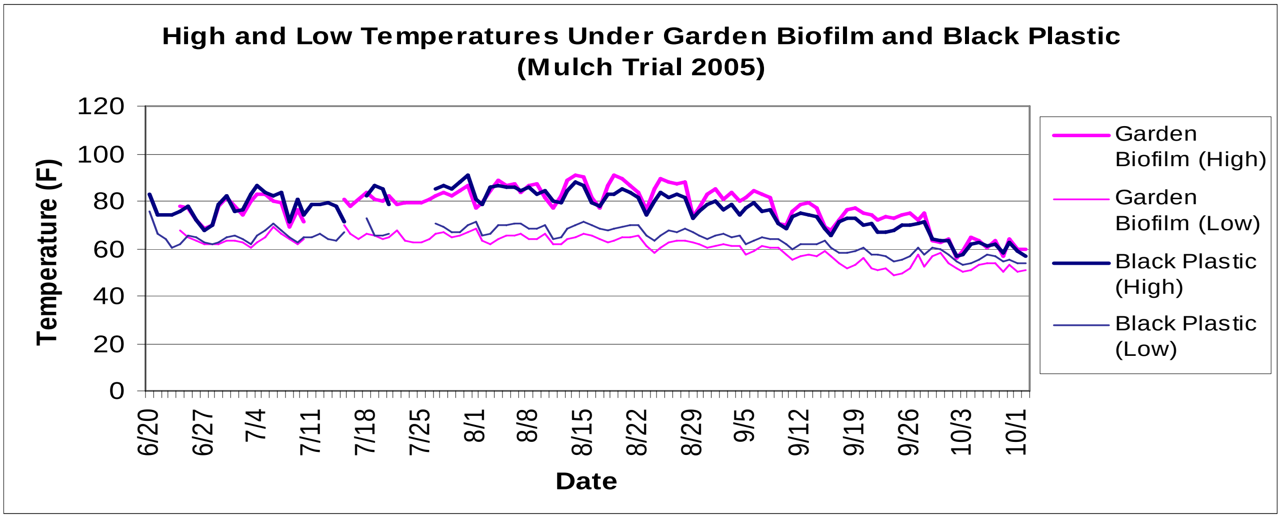


Figure 8. Temperatures (^{o}F) measured under black plastic and under Envirocare 2 mulch in 2005 and 2006.



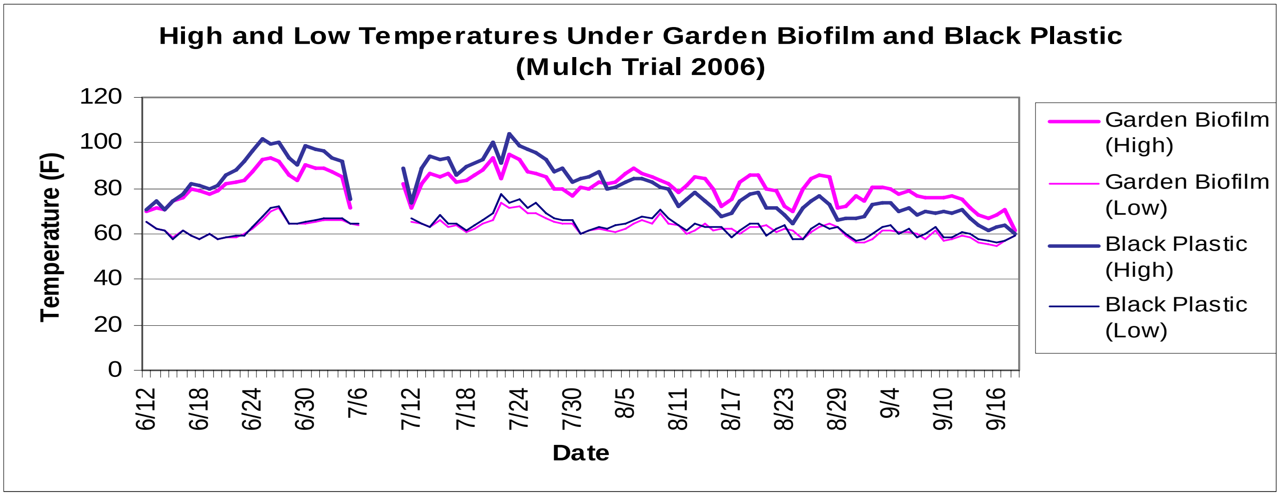
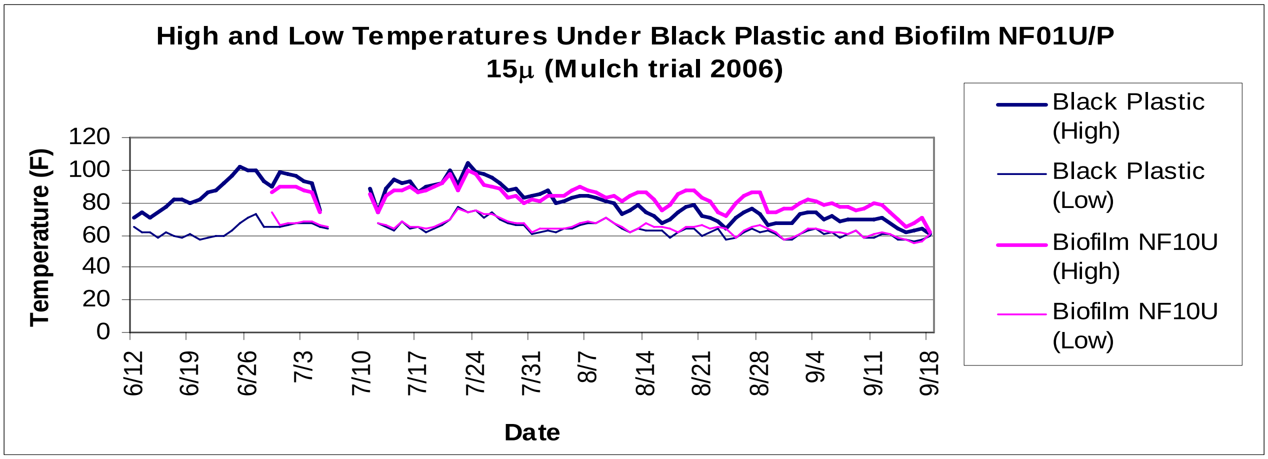
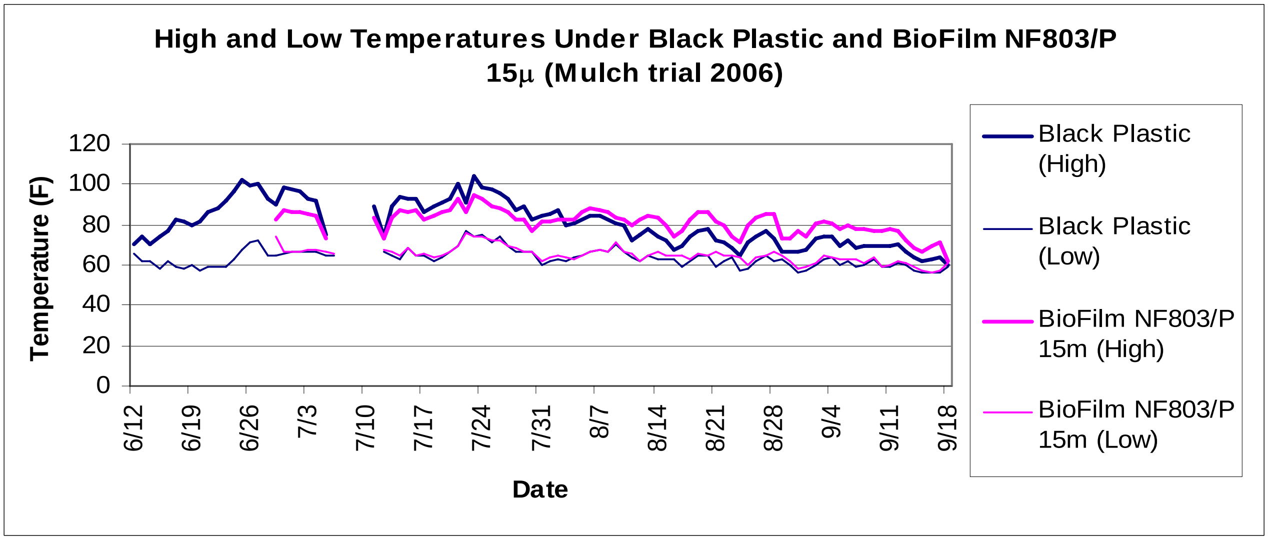


Figure 9. Temperatures (^{o}F) measured under black plastic and under Garden Biofilm mulch in 2005 and 2006.





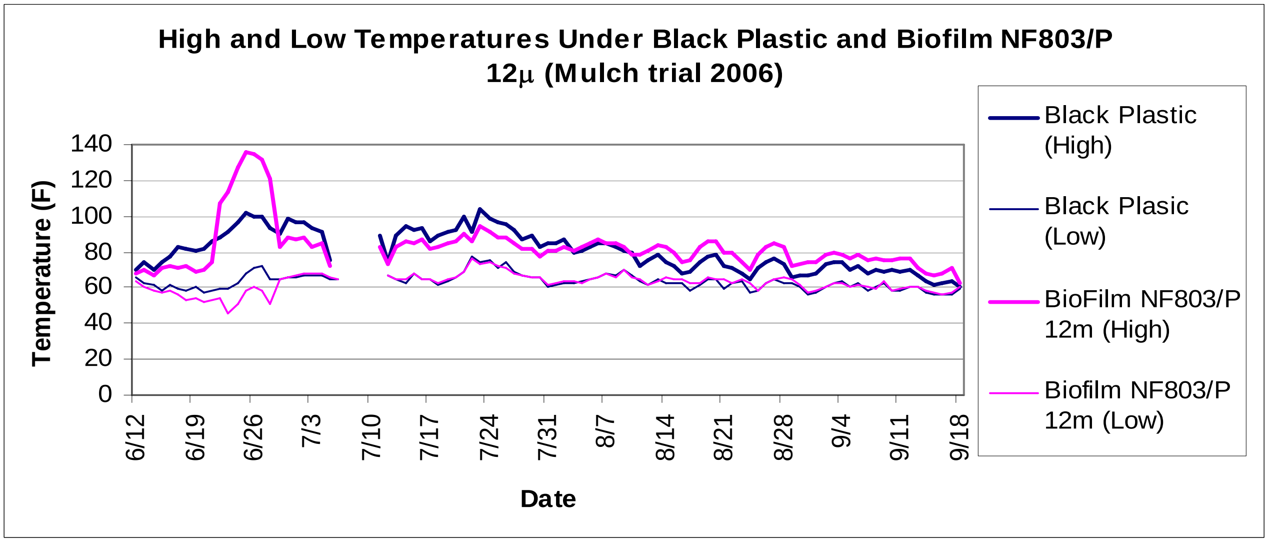


Figure 10. Temperatures (^{o}F) measured under three new Garden Biofilm products and compared to Black plastic in 2006.

Alternatives to Plastic Mulch in Vegetable Production Systems

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Introduction

Since its introduction in the 1950s, plastic mulch has become a standard practice used by many farmers to control weeds, increase crop yield, and shorten time to harvest (Lamont, 1991). Plastic mulch has contributed significantly to the economic viability of farmers worldwide, and by 2006 it was estimated that 400,000 acres were covered with plastic mulch in the United States (American Plastics Council, 2004; Takakura and Fang, 2001; Bergholtz, 2006) and 1,800 acres in Washington. Due to tracking difficulties it is impossible to accurately determine the true number of acres. (Garthe, 2006). Each year farmers must dispose of their plastic and the disposal option that most choose is the landfill (Garthe, 2002). Many small-scale and organic farmers choose not to use plastic mulch because of the waste disposal issues. Ideally, farmers would like to plow down the mulch at the end of the season, thereby eliminating removal as well as disposal costs (Sorkin, 2006). Degradable plastics were introduced in the 1980's; however, there remain many questions regarding their efficacy, degradability, and potential residues (Vert *et al*., 1992; Riggle, 1998; Shogren, 2000; Hockmuth, 2001). For organic farming, degradable mulches would need to meet National Organic Program (NOP) standards.

The purpose of this study was to identify and test degradable mulch products that can be used as effective and affordable alternatives to standard plastic mulch. We conducted the study over a four year period, 2004-2007. In the first two years new products were developed and tested (Miles *et.al*., 2005), and in the second two years the most promising products were evaluated. In all years, degradable mulches were tested with four different vegetable crops in an organic vegetable production system to evaluate mulch durability and effects on soil temperature and crop yields. Different vegetable crops have different temperature needs, and it is possible each crop may perform best with a different mulch product. This is a report for 2006 and 2007.

Materials and Methods

We evaluated 10 alternative mulches in a field study in 2006 and 8 in 2007 (Table 1). Both years, all alternative mulch products were compared to black plastic mulch. In 2006, the study was conducted in a field that was managed organically, and in 2007 the study was conducted in a field that was certified organic. Some of the products tested may not currently be allowed in organic systems, and research such as this study is needed to determine their suitability.

The experimental design both years was a randomized complete block with four replications. Main plots were 55 feet long by 3 feet wide and each included 4 subplots, one for each of 4 vegetable crops. Vegetable crops were selected to represent 2 growing periods (short vs. long) and 2 temperature regimes (cool vs. warm): lettuce – short growing season, cool temperature; broccoli – long growing season, cool temperature; bell pepper – short growing season, warm temperature; and icebox watermelon – long growing season, warm temperature. Plants were seeded in the greenhouse mid-April both years, and transplanted into the field June 9 2006, and May 23 (lettuce), June 12 (peppers and watermelon) and June 24 (broccoli) in 2007. "Pirat" lettuce, "Gypsy" broccoli, and "California Wonder" bell peppers were planted in double 10-foot-long rows, while "Smile" in 2006 and "Triple Play" in 2007 icebox watermelon was planted in a single 21-foot long row. Spacing in the row was 12 inches for lettuce (20 plants per plot), 20 inches for broccoli and peppers (8 plants per plot), and 3 feet for watermelon (6 plants per plot) (Figure 1).

Table 1. Descriptions of mulch products evaluated in 2006 and 2007 at Washington State University Vancouver REU. This table is not intended to be used to promote any products listed or detract from any products not included in this field study.

Product	Description	Year Tested
Black plastic (control)	1.0 mil embossed black polyethylene plastic film	2006, 2007
Envirocare 1	Black plastic w/ Ciba Envirocare TDPA (Totally Degradable Plastic Additive); 75 days to degradation	2006
Envirocare 2	Black plastic w/ Ciba Envirocare TDPA (Totally Degradable Plastic Additive); 140 days to degradation	2006
Garden Biofilm	Cornstarch-based black film, 100% degradable;	2006, 2007
Garden Biofilm NF01U/P 15 mic	Cornstarch-based black film, 100% degradable; developed for short cycle crops	2006, 2007
Garden Biofilm NF803/P 12 mic	Cornstarch-based black film, 100% degradable; developed for longer cycle crops	2006, 2007
Garden Biofilm NF803/P 15 mic	Cornstarch-based black film, 100% degradable; developed for longer cycle crops	2006, 2007
Planters Paper	Kraft paper with black pigment; 100% recycled fiber	2006, 2007
LF 4	Bag Paper - normally sized, no wet strength; 40% recycled fiber	2006
LF 5	Hi STFI Liner (Hi Performance Liner); medium sized, medium wet strength, 18% recycled fiber	2006, 2007
Black LF 5	Hi STFI Liner (Hi Performance Liner); medium sized, medium wet strength, 18% recycled fiber, coated with black carbon	2007

Mulches were laid using a mulch layer tractor attachment. Drip tape was laid under the plastic at the same time as the mulch. After laying the mulches, holes were manually punched using a bulb setter and vegetables were transplanted by hand. Plots were drip irrigated once a week at the rate of 1 inch. Seedlings were fertilized in the greenhouse with Biogan soluble fish powder (12-2-1) in 2006 and BioLink (5-5-5) in 2007, and soluble seaweed extract powder (Acadian 1-0-4 w/ trace minerals) both years. Plants were fertigated in the field immediately after transplanting and every 3 weeks thereafter for a total of four applications. In 2006, Biogan soluble fish powder (12-2-1), Biolink (5-5-5), and Acadian soluble seaweed extract powder were applied at the lowest label rates, and total N applied was 1.09 lbs N/A. In 2007, fertilizer PAR4 (9-3-7) was applied to beds prior to transplanting at the rate of 87 lbs N per acre. Plants were fertigated at transplanting and every 3 weeks thereafter (total of four applications) with BioLink (14-0-0), seaweed extract powder (Acadian 1-0-4 w/ trace minerals), and BioLink Boron (2-0-0, 3% B) at the rate of 48.36 or 25.42, 5.34 and .016 lbs N/A, respectively.

Temperatures were measured with Hobo field monitors at the soil surface beneath each mulch product, and at a 2-inch depth in the neighboring bare soil. Mulch quality was rated weekly on a scale of 0 to 9 where 0 was 0-9% mulch cover and 9 was 90-100% cover. Vegetables in each plot were harvested when they reached peak maturity, and yield measurements included marketable yield, number of marketable fruits/heads, and number of days to first harvest. In 2006, Envirocare 1 and Envirocare 2 were removed from the field at the same time as black plastic and all other products were tilled into the soil.

Figure 1. Field trial of alternatives to plastic mulch at WSU Vancouver REU in 2006.

Results and Discussion

Mulch durability. Mulch products evaluated in this study showed significant differences in quality (durability) over time (Figure 2). Both years, black plastic was the most durable mulch. Envirocare 1 and 2 in 2006 were as durable as black plastic, but had negligible degradability when tilled into the soil or composted (Miles *et al.*, 2006). LF 5 was the most durable alternative product, with quality declining by less than 20% in 2006 over the course of the growing season. In 2007, quality of LF 5 declined more rapidly than for several other alternative mulch products, although final rating was slightly higher than for others. Durability of Black LF5 was slightly lower than regular LF 5 but not significantly different. Weed growth under the LF 4 paper mulch in 2006 was the primary cause of its decline in quality. Planters paper had relatively good durability in 2006 while in 2007 durability was low. Of the corn starch products, Garden Biofilm NF01U/P15 and Garden Biofilm NF803/P15 were the most durable both years while Garden Biofilm NF803/P12 and Garden Biofilm were the least durable.

Crop yield. Yields differed significantly between years and were lower for all crops in 2006 than in 2007 (Tables 2, 3, 4 and 5). In 2006, yields with paper mulches tended to be lower than with other mulch products, and these differences were significant for some crops. Of the paper mulches, LF 4 degraded the earliest and yields were subsequently lower than for all other products. In 2007, there was little difference in crop yield due to mulch product. Watermelon were impacted by poor pollination throughout all plots, likely due to competition for pollinators with a neighboring watermelon crop.

In 2006, yield, number of heads and head weight of lettuce was not significantly impacted by mulch product (Table 2). Number of broccoli heads were greatest with Envirocare 2 and Garden Biofilm, and lowest with Garden Biofilm NF01U/P15 (Table 3). Average head weight of broccoli was greatest with Garden Biofilm NF803/15 and lowest with black plastic and Garden Biofilm. Pepper yield and number of fruit were greatest with Garden Biofilm NF803/15 and lowest with LF 4 (Table 4). Watermelon yield, fruit number, and average fruit weight were greatest with Envirocare 1 and Garden Biofilm NF01U/P15, and lowest with LF 4 and LF 5 (Table 5).

In 2007, yield, number of heads and head weight of lettuce and broccoli were not significantly affected by mulch product (Tables 2 and 3). Pepper yield was greatest with black plastic, Garden Biofilm NF01U/P15, Garden BiofilmNF803/15, and Garden Biofilm803/12, and lowest with Black LF 5, LF 5, Planters Paper, and Garden Biofilm (Table 4). Watermelon yield was not impacted by mulch product, most likely due to overall low pollination in this crop throughout all plots (Table 5).

Days to crop maturity. Mulch products had a significant effect on days to maturity for all crops except peppers in 2006, however these effects were generally not consistent (Table 6). Garden Biofilm NF01U/P15 and Garden Biofilm NF803/15 resulted in earlier maturity in lettuce, but later maturity in broccoli and watermelon. Garden Biofilm and Envirocare 1 resulted in earlier maturity in watermelon while LF 4 and LF 5 resulted in later maturity. In 2007 days to maturity of all crops were not significantly affected by mulch product.

Temperature under mulch. Both years, maximum temperatures under all products compared to black plastic tended to be more different than minimum temperatures (Figures 3-10). Maximum temperatures under LF5 varied early in the season (fluctuated from lower to higher to lower) but were equivalent to black plastic from August onwards. Maximum temperatures under Black LF5 were greater than black plastic from August onwards while minimum temperatures were lower. Under Planters paper, maximum temperatures were somewhat equivalent as under black plastic early in the season but were higher later in the season. Maximum and minimum temperatures under Garden Biofilm, Garden Biofilm NF01 U/P15, Garden Biofilm NF803/PU15 were very similar to black plastic both years.

Conclusions

In this study, once mulch cover fell below 50% (a quality rating of 5 or below), the product was ineffective for weed control. Both years Garden Biofilm and Garden Biofilm NF803/P12 reached a rating of 5 by early August while all other degradable mulch products reached a rating of 5 by early to mid September in one year only. Preliminary results indicated that LF 5 was the most durable of all alternative mulches tested, however, durability was significantly lower in the second year of this study. More testing may be needed to determine the expected durability of LF 5 under variable field conditions.

In general, yield of lettuce and broccoli (both cool season crops) were least impacted by paper mulch whereas yield of pepper and watermelon (both warm season crops) were more greatly impacted. Thus, paper mulch products may be more suitable for cool season crops and not as well suited for warm season crops. Temperatures under LF 5 were variable early in the season as compared to under black plastic and this may have contributed to decreased crop yield. Of the cornstarch products, Garden Biofilm

NF01U/P15 and Garden Biofilm NF803/P15 appeared somewhat durable in the field and had the added benefit of resulting in high crop yields.

Ideally, a degradable mulch would degrade in the soil, eliminating the removal and disposal costs. In this study, cornstarch and paper mulches were tilled into the soil at the end of the season and by the following spring, they had broken down to the point where residues were no longer visible to the naked eye. Envirocare 1 and Envirocare 2 were as durable as black plastic in the field and resulted in similar crop yield. However, Envirocare products did not degrade when they were incorporated into the field or when they were incorporated into on-farm compost piles. Therefore these products did not provide reduced farm labor costs or disposal fees. In addition, our organic certifier, WSDA Organic Food Program, determined that these products were not allowable for use in certified organic crop production systems.

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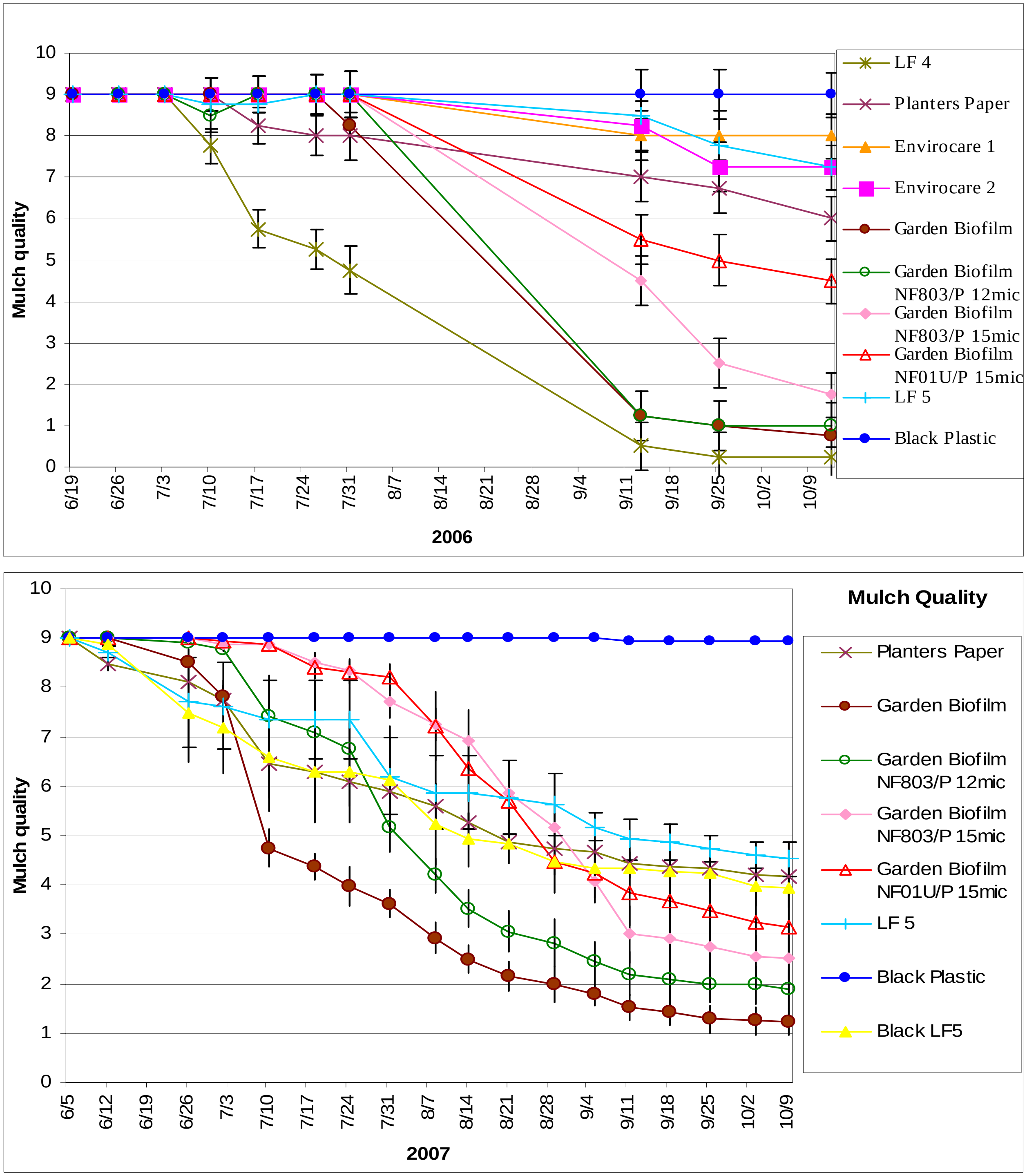


Figure 2. Mulch durability (quality over time) on a scale 0-9, where 0 is 0-9% mulch cover and 9 is 90-100% cover, in 2006 and 2007 at WSU Vancouver REU.

Table 2. Mean marketable yield (kg) of lettuce, number of marketable heads per plot, and weight per head (g) in 2006 and 2007.

Mulch Product	Yield (kg)		No. Heads		Head Wt. (g)	
	2006	2007	2006	2007	2006	2007
Black plastic	2.14 a	9.14 a	16 a	20 a	135 a	457 a
Envirocare 1	2.59 a		16 a		162 a	
Envirocare 2	2.86 a		17 a		171 a	
LF 4	2.31 a		16 a		142 a	
LF 5	2.73 a	9.07 a	17 a	20 a	162 a	451 a
Black LF 5		8.56 a		19 a		428 a
Planters Paper	2.43 a	8.61 a	16 a	19 a	154 a	430 a
Garden Biofilm	2.20 a	8.60 a	20 a	20 a	125 a	429 a
Garden Biofilm NF803/12	2.62 a	10.90 a	17 a	20 a	154 a	544 a
Garden Biofilm NF01U/P15	2.33 a	10.21 a	18 a	20 a	131 a	510 a
Garden Biofilm NF803/15	2.33 a	8.67 a	16 a	20 a	144 a	433 a
P Value	**0.6475**	**0.7576**	**0.8960**	**0.3611**	**0.2336**	**0.7585**

Table 3. Mean marketable yield (kg) of broccoli, number of marketable heads per plot, and weight per head (g) in 2006 and 2007.

Mulch	Yield (kg)		No. Heads		Head Wt. (g)	
	2006	2007	2006	2007	2006	2007
Black plastic	1.18 a	7.35 a	8.3 abc	7.5 a	137 d	919 a
Envirocare 1	1.50 a		8.8 ab		164 cd	
Envirocare 2	1.78 a		9.8 a		183 bcd	
LF 4	1.25 a		7.8 abcd		162 cd	
LF 5	1.14 a	7.52 a	6.3 cd	8.0 a	188 bcd	939 a
Black LF 5		6.50 a		8.3 a		813 a
Planters Paper	1.15 a	7.23 a	7.8 abcd	7.5 a	150 cd	903 a
Garden Biofilm	1.29 a	7.30 a	9.5 a	8.0 a	137 d	913 a
Garden Biofilm NF803/12	1.66 a	7.41 a	6.5 bcd	8.3 a	258 ab	926 a
Garden Biofilm NF01U/P15	1.36 a	7.54 a	5.8 d	7.8 a	234 abc	943 a
Garden Biofilm NF803/15	2.03 a	7.10 a	6.5 bcd	8.0 a	318 a	881 a
P Value	**0.2506**	**0.9704**	**0.0167**	**0.4694**	**0.0032**	**0.9704**

Table 4. Mean marketable yield (kg) of pepper, number of marketable fruit per plot, and weight per fruit (g) in 2006 and 2007.

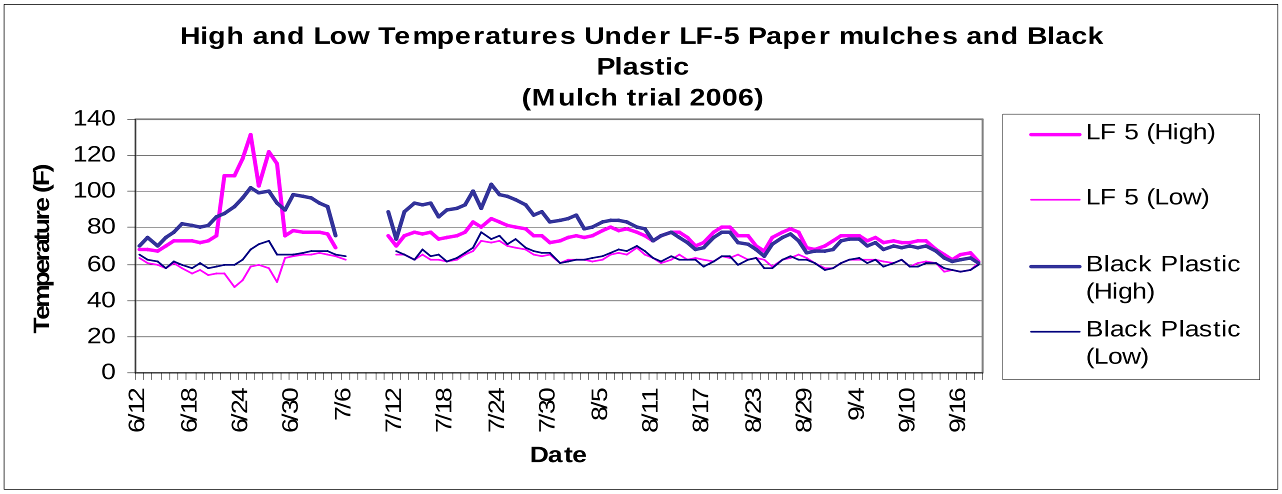
	Yield (kg)		No. Fruit		Fruit Wt. (g)	
Mulch	**2006**	**2007**	**2006**	**2007**	**2006**	**2007**
Black plastic	1.86 abc	8.01a	15.8 abc	35.3 a	114 a	203 a
Envirocare 1	3.31 ab		27.8 ab		118 a	
Envirocare 2	3.70 ab		29.5 ab		126 a	
LF 4	0.40 c		3.8 c		107 a	
LF 5	2.11 abc	4.29 bc	19.0 abc	23.0 a	111 a	181 a
Black LF 5		3.54 c		20.0 a		175 a
Planters Paper	1.51 bc	4.83 bc	13.8 bc	21.5 a	113 a	188 a
Garden Biofilm	2.67 abc	5.12 bc	21.0 abc	30.5 a	129 a	175 a
Garden Biofilm NF803/12	2.52 abc	5.69 ab	18.8 abc	34.3 a	159 a	169 a
Garden Biofilm NF01U/P15	3.01 ab	6.47 ab	27.8 ab	27.0 a	108 a	174 a
Garden Biofilm NF803/15	4.09 a	5.85 ab	34.0 a	33.3 a	119 a	166 a
P Value	**0.0002**	**0.0396**	**0.0003**	**0.2544**	**0.4957**	**0.1119**

Table 5. Mean marketable yield (kg) of watermelon, number of marketable fruit per plot, and weight per fruit (g) in 2006 and 2007.

	Yield (kg)		No. Fruit		Fruit Wt. (kg)	
Mulch	**2006**	**2007**	**2006**	**2007**	**2006**	**2007**
Black plastic	11.4 ab	15.3 a	6.5 ab	2.5 a	1.7 ab	6.1 a
Envirocare 1	27.3 a		12.8 a		2.2 a	
Envirocare 2	20.2 ab		10.8 ab		2.0 ab	
LF 4	1.9 b		1.5 b		1.3 ab	
LF 5	6.6 b		6.5 ab		1.1 b	
Black LF 5						
Planters Paper	10.5 ab	6.7 a	6.8 ab	1.3 a	1.4 ab	4.7 a
Garden Biofilm	14.6 ab	8.9 a	8.3 ab	1.6 a	1.8 ab	5.3 a
Garden Biofilm NF803/12	12.7 ab	13.9 a	8.5 ab	2.5 a	1.5 ab	5.5 a
Garden Biofilm NF01U/P15	18.0 ab	11.5 a	13.8 a	2.0 a	1.3 ab	6.3 a
Garden Biofilm NF803/15	18.7 ab	7.4 a	11.0 ab	1.3 a	1.7 ab	5.8 a
P Value	**0.0023**	**0.2606**	**0.0077**	**0.4043**	**0.0471**	**0.7294**

Table 6. Days after transplanting to first harvest of lettuce, broccoli, pepper and watermelon at WSU Vancouver REU in 2006 and 2007.

	Lettuce		Broccoli		Pepper		Watermelon	
Mulch	**2006**	**2007**	**2006**	**2007**	**2006**	**2007**	**2006**	**2007**
Black plastic	39 a	32 a	71 bc	57 a	109 a	97 a	72 abcd	100 a
Envirocare 1	39 a		67 c		109 a		65 d	
Envirocare 2	39 a		67 c		109 a		67 cd	
LF 4	40 a		69 bc		113 a		81 a	
LF 5	38 a	29 a	70 bc	58 a	109 a	94 a	78 a	100 a
Black LF 5		30 a		57 a		90 a		100 a
Planters Paper	39 a	30 a	70 bc	57 a	109 a	94 a	69 bcd	100 a
Garden Biofilm	38 a	30 a	68 c	61 a	109 a	84 a	65 d	100 a
Garden BiofilmNF803/12	34 b	30 a	74 bc	61 a	112 a	78 a	77 ab	100 a
Garden BiofilmNF01U/P15	35 b	29 a	84 a	58 a	109 a	82 a	68 cd	100 a
GardenBiofilmNF803/15	34 b	29 a	84 a	58 a	109 a	77 a	74 abcd	99 a
P Value	**0.0000**	**0.6331**	**0.0000**	**0.6912**	**0.124**	**0.313**	**0.0100**	**0.4414**



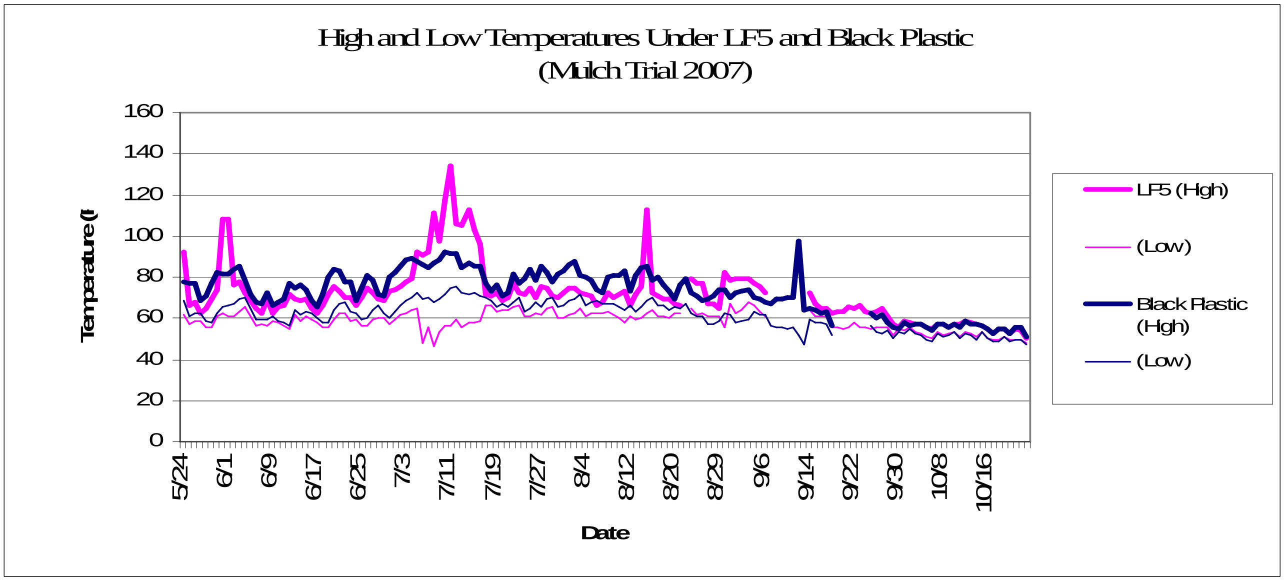
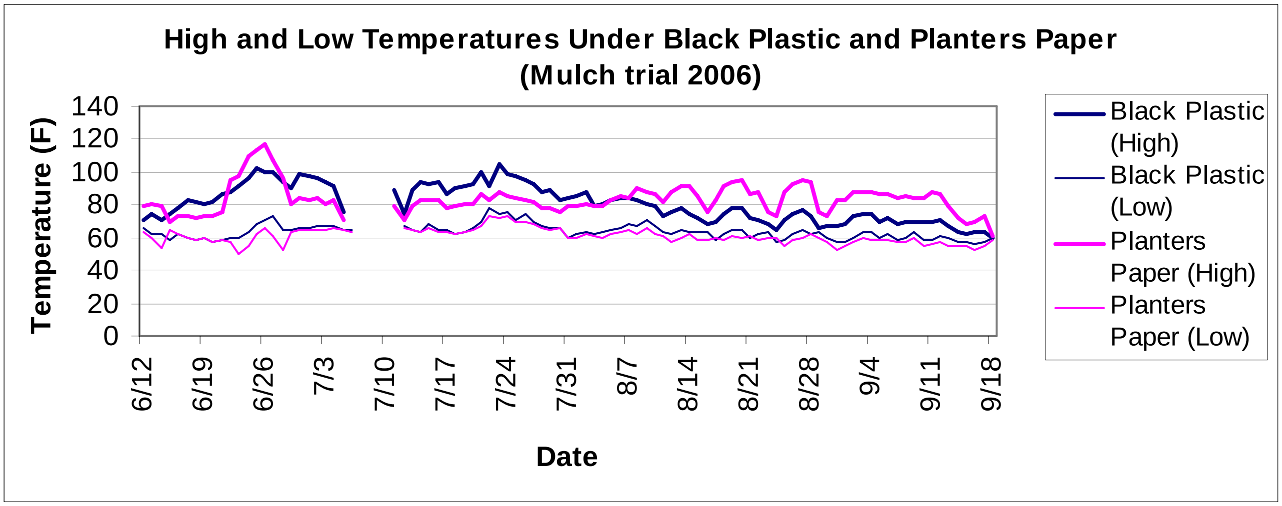


Figure 5. Temperatures (^{o}F) measured under black plastic and under LF 5 paper mulch in 2006 and 2007.



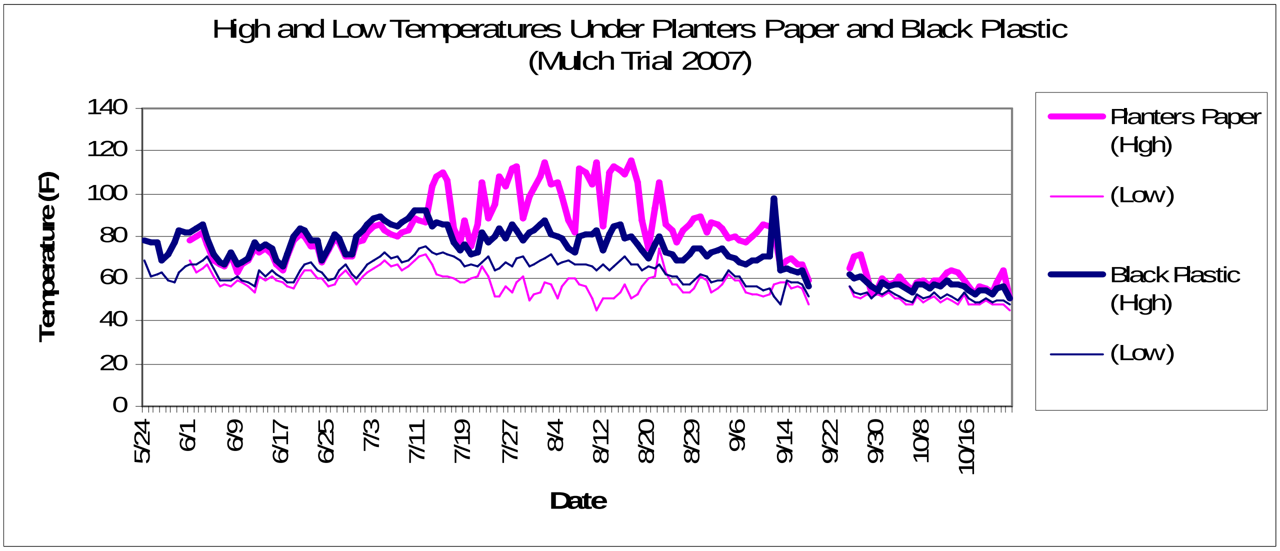
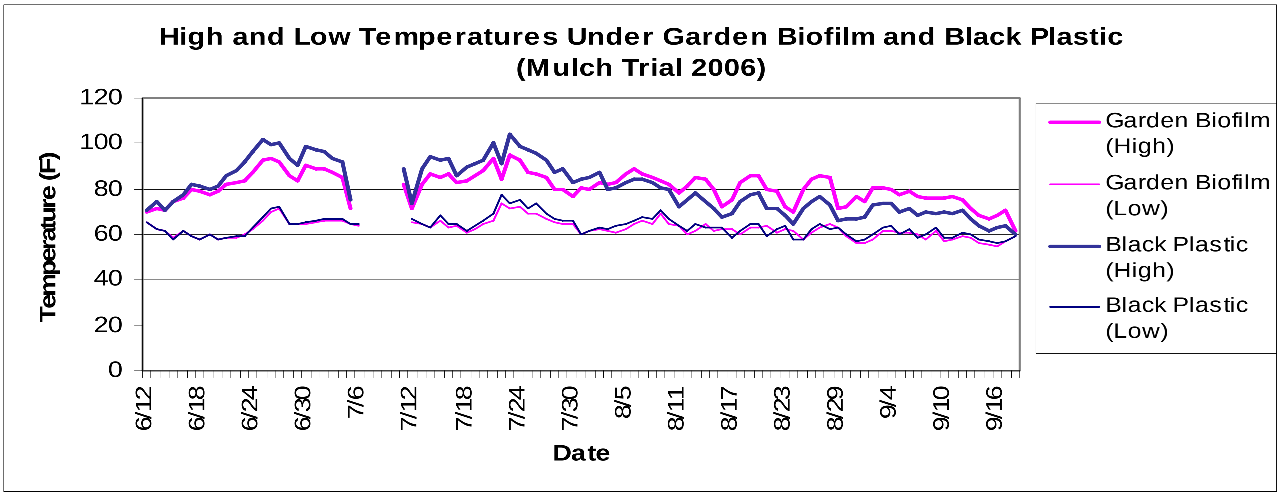


Figure 6. Temperatures (^{o}F) measured under black plastic and under Planters Paper mulch in 2006 and 2007.



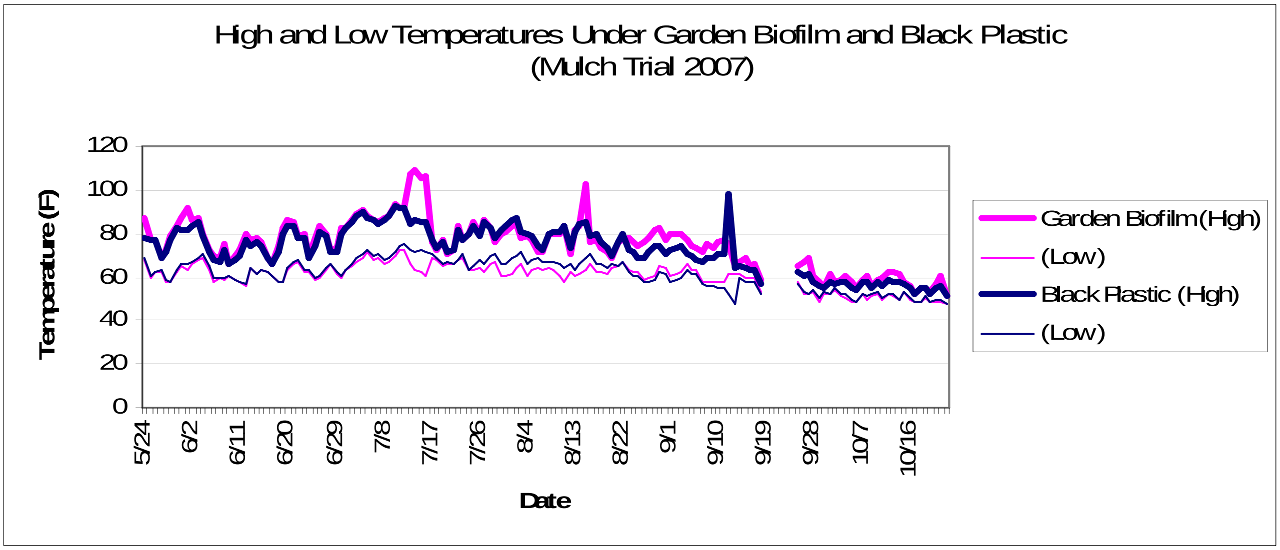
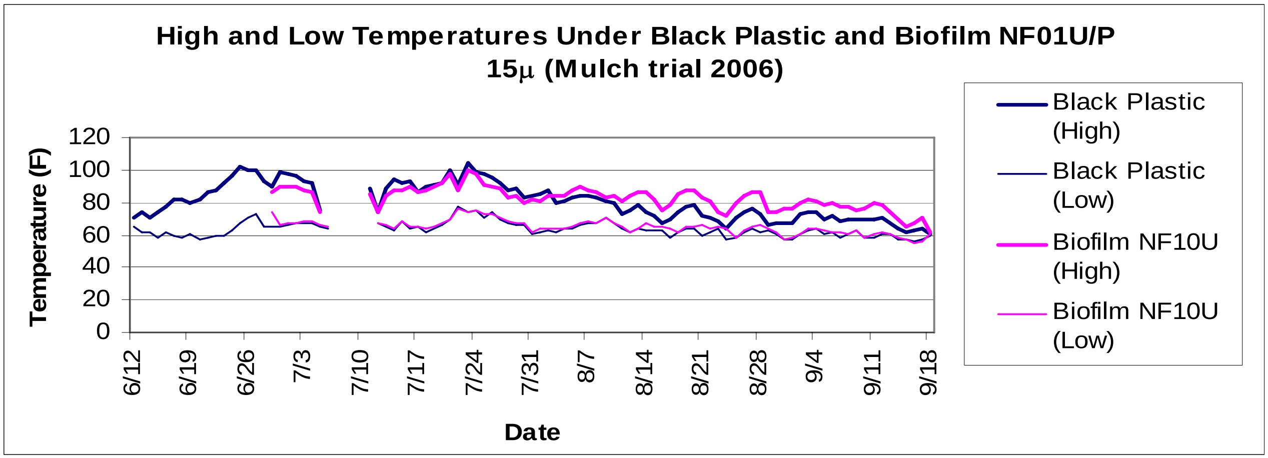
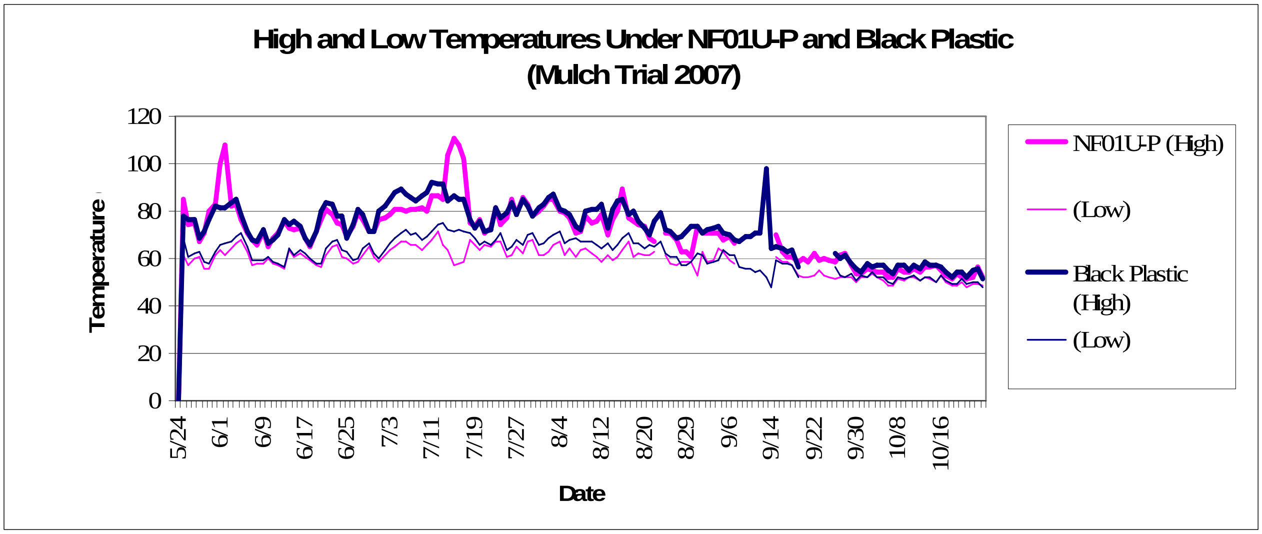


Figure 9. Temperatures (^{o}F) measured under black plastic and under Garden Biofilm mulch in 2006 and 2007.


High and Low Temperatures Under Black Plastic and Biofilm NF01U/P 15µ (Mulch trial 2006)
Temperature (F)
120
100
80
60
40
20
0
6/12
6/19
6/26
7/3
7/10
7/17
7/24
7/31
8/7
8/14
8/21
8/28
9/4
9/11
9/18
Date
Black Plastic (High)
Black Plastic (Low)
Biofilm NF10U (High)
Biofilm NF10U (Low)


High and Low Temperatures Under NF01U-P and Black Plastic (Mulch Trial 2007)
Temperature
120
100
80
60
40
20
0
5/24
6/1
6/9
6/17
6/25
7/3
7/11
7/19
7/27
8/4
8/12
8/20
8/29
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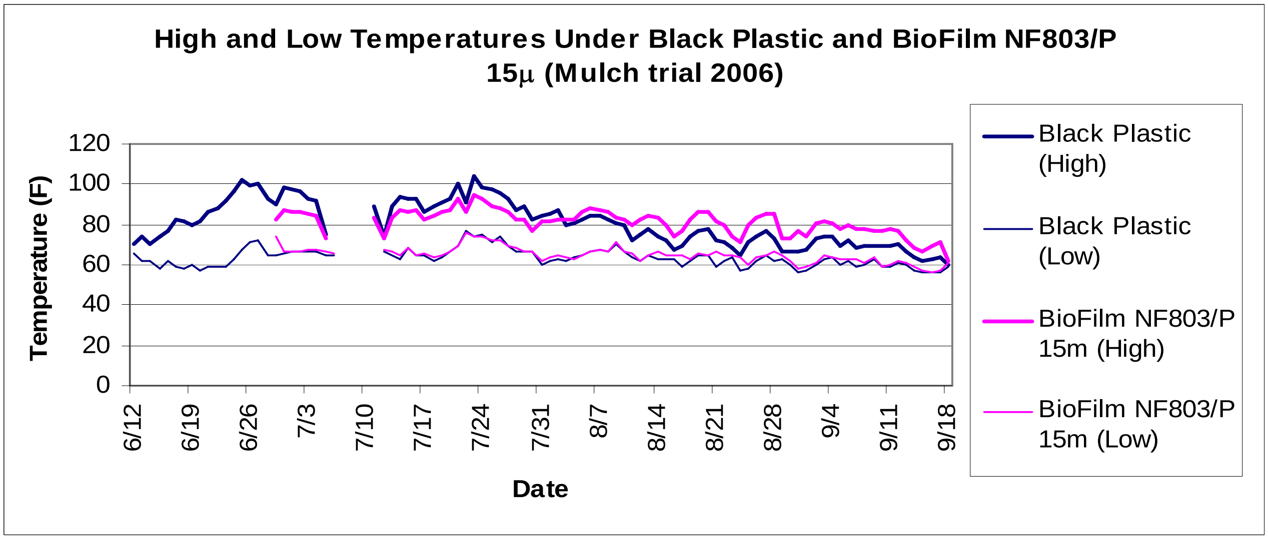
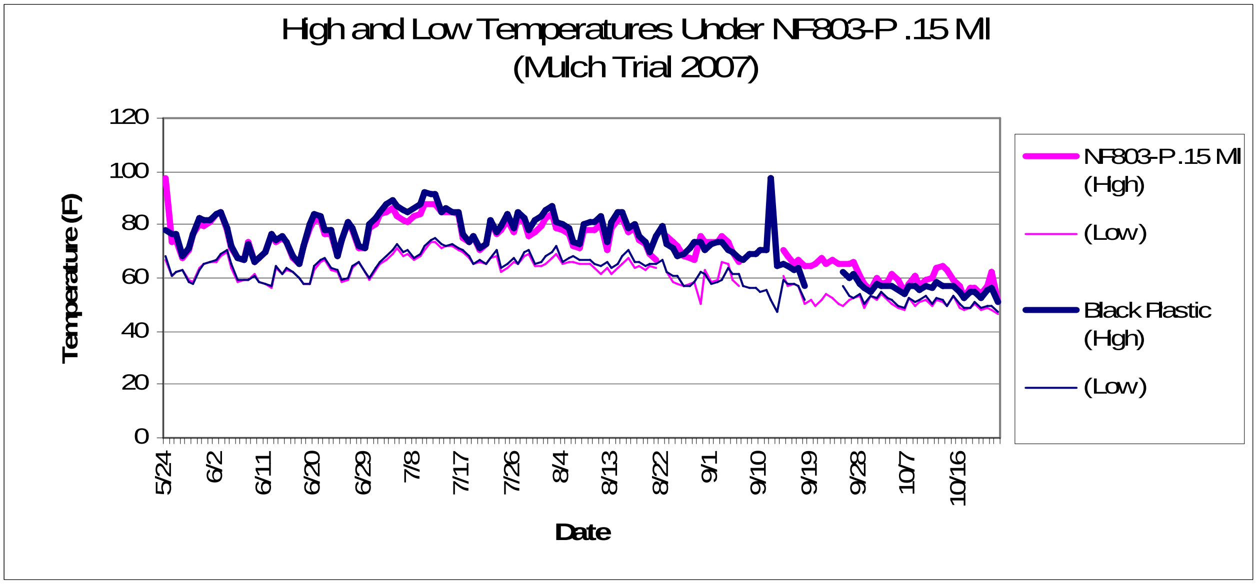
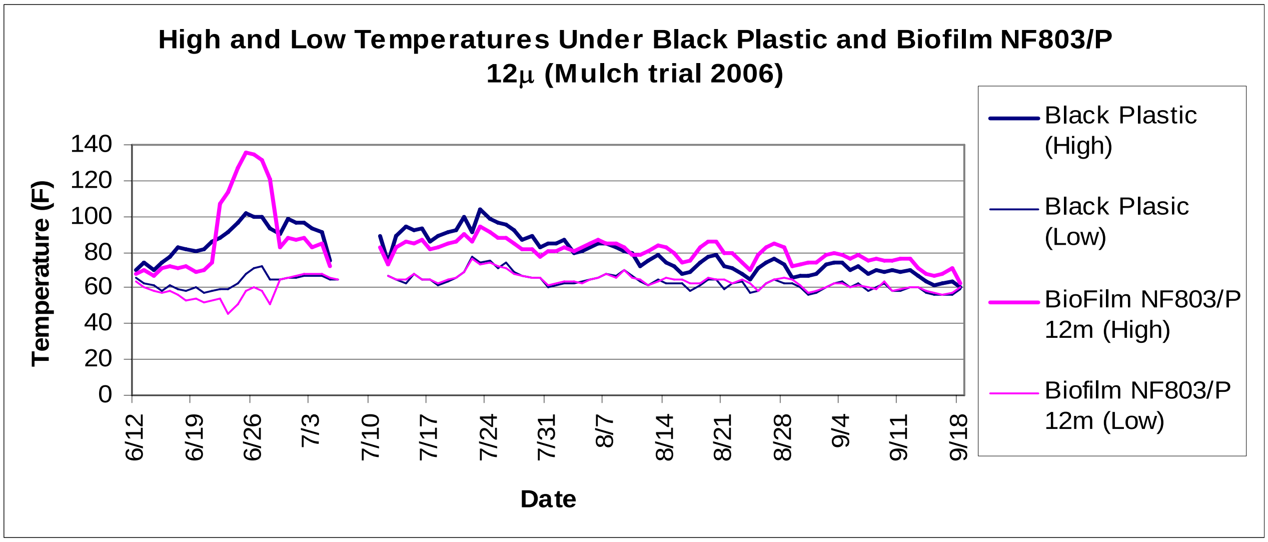
Date
NF01U-P (High)
(Low)
Black Plastic (High)
(Low)


High and Low Temperatures Under Black Plastic and BioFilm NF803/P 15µ (Mulch trial 2006)


High and Low Temperatures Under NF803-P .15 Ml (Mulch Trial 2007)



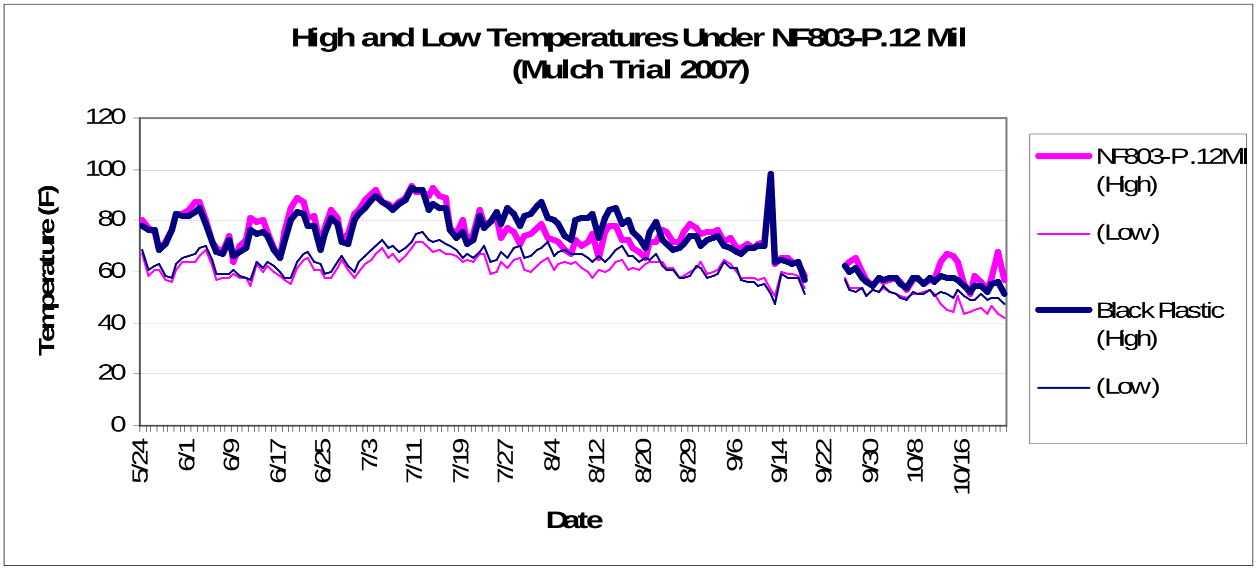


Figure 10. Temperatures (^{o}F) measured underneath three new Garden Biofilm products and compared to Black plastic in 2006 and 2007.

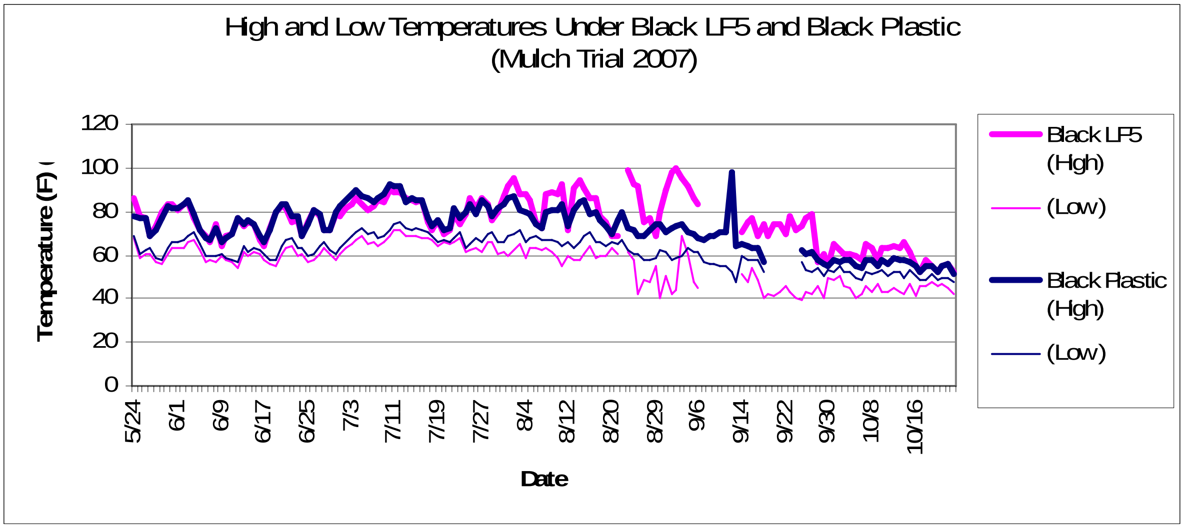


Figure 11. Temperatures (^oF) measured underneath Black LF5 compared to Black plastic in 2007.

A comparison of biodegradable mulches to black plastic mulch

2006 Final Report

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Summary

A Comparison of Biodegradable Mulches

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Introduction

Both conventional and organic farmers rely on plastic mulch to control weeds, heat the soil and retain nutrients. While it is very effective in all these areas, there is concern over the amount of waste generated when the plastic is pulled out of the fields at the end of the season. A material that provides the above-mentioned benefits but is biodegradable in addition would eliminate the concern of ever-increasing agricultural pollution. To date, some biodegradable materials have been introduced to the market as alternatives to plastic but little has been written comparing their efficacy and, just as important, their cost to a small farmer.

This experiment was designed to compare yield and cost of three materials: black plastic, a cellulose-based biodegradable film called Agrofilm and paper mulch. While the black plastic is less expensive per foot than the other two films, labor hours must be spent to remove the plastic at the end of the season and disposal fees can further reduce profits. A higher yield with the plastic, however, may tip the scales in favor of continuing its use. It is our hope that recording the costs and yields for several crops with all three materials will make the decision of whether to try a biodegradable mulch easier for a farmer who would like an alternative to plastic.

Farm Profile

Cave Moose Farm is a certified organic, diverse vegetable and flower farm. We grow bedding plants in the spring and then field and greenhouse cultivated crops in the summer and fall. In addition we produce log-grown shiitake mushrooms from June through October. We sell to our Community Supported Agriculture (CSA) program, The Burlington Farmer's market, restaurants and local stores. We have six acres of fields for annual crops and two acres of perennial crops such as berries and flowers. This year we have discontinued the CSA and will be focusing mostly on markets and wholesale; a decision based on the need to reduce labor costs.

Participants

Our technical advisor was Vern Grubinger who visited the site several weeks after the experiment began and gave technical advice throughout the season via email. A crew of three and I carried out the experiment from May through October of 2005.

Project Activities

The experiment was conducted in three different plots randomly selected throughout a six-acre field. The soil type is clay-loam amended with compost in most areas and a pH on average of 6.5. Each plot has one row of plastic adjacent to one row of Agrofilm adjacent to one row of Kraft Paper.

Plot one and two were planted May 20. Plot one consisted of 91 feet of Expert pumpkin planted two plants per hole, every two feet. The remainder of the row (71 feet) was planted with Baby Pam pumpkin, two plants per hole every two feet. The plants were treated with fish emulsion upon planting and ½ cup of Pro-gro was incorporated into the planting hole.

Plot two was planted with 75 feet of Bush Delicata winter squash; two plants per hole, two feet apart; and 95 feet of Metro Butternut squash, two plants per hole, two feet apart. The winter squash were also treated with fish emulsion before planting with an additional ½ cup Pro-gro incorporated into the soil.

Plot three was planted June 3 with 160 feet of Festival watermelon, two plants per hole, two feet apart. A mix of ½ cup Pro-gro and greensand was added to each planting hole upon planting.

Overhead irrigation was provided periodically as needed throughout the summer to each plot. One application of liquid fish and seaweed fertilizer was given in mid-summer.

Hours required to lay each material were recorded as were extra hours needed to fix any of the rows. Given that the machinery always needs to be adjusted many times for the first installment of any new roll, the time taken to lay each material was taken in aggregate for all three plots and divided by three for each of the materials.

Yields from each crop from each material were recorded. Time necessary to remove the plastic at the end of the season was also recorded. Costs per foot for each material as well as disposal fees for the plastic were figured into the final cost analysis.

Economic Results

These figures are based on labor costs (which include hourly wage, taxes, and workers' compensation) at $20/hr. Disposal of the plastic was $15/yd. The plastic cost $73 for a 4' x 2000' roll. The BioBag Agrofilm cost $335 for a 4' x 4000' roll. The paper cost $200 for a 4' x 1500' roll. All of the above costs include shipping.

Cost per foot = Cost of materials + time in labor for laying and maintaining

Pumpkins: Plastic $0.21/foot
Agrofilm $0.19/foot
Paper $0.35/foot

Winter squash: Plastic $0.20/foot
Agrofilm $0.19/foot
Paper $0.34/foot

Watermelon: Plastic $0.21/foot
Agrofilm $0.20/foot
Paper $0.35/foot

Yield per dollar spent

Pumpkins: Plastic 2.71 lbs/$
Agrofilm 3.19 lbs/$
Paper 0

Winter squash Plastic 2.98 lbs/$
Agrofilm 1.78 lbs/$
Paper 0

Watermelon Plastic 11.16 lbs/$
Agrofilm 6.2 lbs/$
Paper .78 lbs/$

Conditions

Conditions were very good for farming in the summer of 2005. The only factor that may have affected the results was that our soil is still not at a fertility level we would like which resulted in lower yields than ideal.

Assessment

The cost per foot of the Agrofilm and plastic were very close. Though the Agrofilm is more expensive, the hours necessary to remove the plastic plus the disposal fees brought the cost of the plastic to slightly higher than the per-foot cost of the Agrofilm. The per-foot cost of the paper was significantly higher than both materials for several reasons. First, the cost of the material itself was comparatively expensive; one and a half times higher than Agrofilm and more than three and a half times higher than plastic. Second, the paper took a great deal more time to lay than the other two materials due to the fact it tore easily using the mulch layer as intended. In fact, after much frustration and torn paper, we had to remove the rear discs that were designed to throw dirt over the edges and instead hoe dirt by hand to tuck it in. After this effort, the paper tore down the middle on plot one and two within two days after a mild breeze caused it to flap. The paper in plot three tore halfway down the row. No effort was made to weed in these rows and consequently there was zero yield in the paper rows of plot one and two and only a small yield in the paper row of plot three. We would not recommend the paper mulch for any application.

The results are less definitive when looking at the yields from the plastic and Agrofilm. The yield per dollar spent was better in the plastic material for winter squash and nearly twice as high for watermelon but higher in the Agrofilm in the pumpkin patch. We have no explanation for these variances except that it is possible that the plastic retained more heat which resulted in larger fruit in the plastic-watermelon row. A study done by Rangarajan, Ingall and Davis, (Alternative Mulch Products 2003, Cornell Univ, Ithica, NY) that compared the two products showed melon yields comparable to black plastic on one farm and nearly as high on another farm growing melons. Where heat is not as much of a factor in the pumpkins and winter squash, the variances may be attributed to local fertility or weed pressure despite our efforts to ensure the same conditions for all of the crops.

Adoption

For farmers looking for a cost-effective alternative to plastic mulch, the Agrofilm is a good option for some crops such as winter squash. The Agrofilm began to degrade noticeably in mid-July and was nearly disintegrated by September. We noted that by the time it disintegrated, it had eliminated weeds below, most likely from heat and smothering, and weeds were not a problem for the remainder of the season. In addition, rather than allotting time to the dreaded job of pulling up dirty plastic in the fall, we simply tilled the remnant crop under and were able to spend the time on other fall chores.

The results in the watermelon plot may give some farmers pause before switching completely away from plastic. Since our results favored plastic for melons in comparison to the study conducted by Rangarajan, et.al, perhaps more studies are called for in different types of crops to determine which crops are a good match for biodegradable mulches. Though we plan to use the biodegradable mulch for squash and possibly flowers next year, we will continue to use the plastic for our melon crops.

We encourage biotech companies to continue research on this topic using renewable resources or natural by-products of other manufacturing processes. I have always theorized that low-grade wool would be and excellent component of a mulch material in that it is insulating, strong but biodegradable and even contains some nutrients. Currently, there is little or no market for low-grade wool so the manufacturing of such a product could provide extra income for sheep farmers as well as a needed commodity to vegetable farmers.

Outreach

We plan to send our results to various agricultural publications so other farmers can decide if switching from plastic is right for their farm.

Summary

Using large quantities of a petroleum-based product that cannot be recycled is antithetical to the principles of sustainable farming. Even if a farmer chose to switch half of her crops over to biodegradable mulch, this would certainly have a positive effect on reducing agricultural pollution and use of non-renewable resources.
We have found that AgroFilm shows comparable yields and nearly the same costs as plastic mulch for two out of the three crops we experimented with. More experiments with other types of crops and other types of materials are needed so farmers can confidently switch from plastic mulch to a biodegradable material. In the meantime, we will switch to the Agrofilm for many of our crops in 2006 and hope to reduce the amount of plastic waste generated at the farm.

Laura Sorkin
March 14, 2006

View this report online: http://mysare.sare.org/mySARE/ProjectReport.aspx?do=viewRept&pn=FNE05-562&y=2006&t=1

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Total Number of Pages : 3

Biodegradable mulches: How well do they work?

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Background

Vegetable growers in New York and the Northeast rely on black plastic mulch film to enhance early growth and total yield of many crops, including cucurbits, peppers and tomatoes. These polyethylene mulch films help growers achieve early, more lucrative markets through improved soil temperatures, water and nutrient availability. A continuing problem with using plastic mulch film, however, is the increasing costs of disposal. Grower estimates of labor to pick up plus charges to dispose of plastic mulch film at a landfill range from $25 to $100 per acre, depending on landfill fees. While black plastic mulch film is relatively inexpensive, biodegradable mulches could be tilled in at the end of the season, reducing labor hours for pick up as well as disposal costs. Biodegradable mulches of interest are those made from plant starches (corn or wheat) and are completely biodegrade in the soil. Soil microorganisms should be able to break down the mulch to carbon dioxide and water, leaving no mulch residues in the soil. Ideally, these mulches would adhere to the soil, so they do not blow off the field as they degrade. Other degradable films have been commercialized, but growers have complained that breakdown is uneven and large pieces may blow off the field, creating litter. These other degradable films may also be made primarily of polyethylene, and degrade very slowly in the environment.

Predicting degradation is the challenge with using biodegradable mulches. Generally, thicker biodegradable mulches should last longer in the field, but our experience has shown that breakdown rates are not always tied to mulch thickness. With biodegradable mulches, the rate of break down is affected by climate (temperature, sunlight and moisture), soil type, crop cover and weed pressure. Ideal conditions for crop growth are also those that will help with the breakdown of biodegradable mulch. Warm temperatures, rainfall and sunlight enhance microbial activity of the soil and speed the breakdown. Soils higher in organic matter will generally have higher microbial activity, leading to faster breakdown. As the crop grows over the mulch, the shading will provide some protection of the mulch against the sun. As the mulch breaks down, weeds that emerge through holes in the mulch will stretch the mulch and speed breakdown.

Our research

For the last several years, we have been evaluating new types of mulches for use in vegetable production. We are interested in finding reliable substitutes for black plastic mulch. Our efforts initially focused on paper mulches, and now we have focused on a biodegradable product. This is very different from the photodegradable products released years ago. This mulch is primarily made of plant starches that can be broken down by microorganisms in either soils or composts. We evaluate soil temperatures, air temperatures above the mulch, crop growth rate and total yield and quality of melons. We use melons as our test crop, based upon their sensitivity to soil warming and responsiveness to black plastic mulch.

Our Results in 2006

Field application of Mater-Bi was similar to black plastic. The products had excellent stretch and soil temperatures were similar early in the season. Mid season plant fresh weights indicate that growth on Mater-Bi mulches was similar to black plastic.

All Mater-Bi products were starting to break down (areas exposed to direct sunlight) at the end of July. Despite some early breakdown, we found no differences in early or total yield with any of the different colors of biodegradable mulch and black plastic mulch. Average fruit size and weight (4.0 lbs) were similar among mulch treatments.

Farmer Comments 2007

Most growers interviewed have used biodegradable and plastic mulches for at least two growing seasons. Four growers are using organic growing practices. A farm in New York used 15,000 feet this year and would like to grow other crops on it in the future. Crops grown were basil, tomatoes, eggplant, peppers, pumpkins, green beans, flowers, muskmelons, watermelons, carrots, zucchini, summer and winter squash, sweet potatoes, cabbage, onions, and early broccoli. Mulch layers are used to apply mulch. All growers were satisfied with how it laid, lasted and dissolved in the field. It is very important to have all tension off the roll when laying unlike plastic. A grower greased the spindle of their mulch layer to ensure the mulch would not stretch excessively during application. A grower in MA observed in fields with higher organic matter mulch broke down more quickly, especially when rye stubble is present. They also found mulch was not strong enough to grow crops with close spacing (onions and garlic) or when stepped on frequently (staked tomatoes). Although another farmer in NY said they grow onions successfully on biodegradable mulch. Another suggestion is to apply mulch early in the day when temperatures are lower to decrease stretching. Stretching tends to cause the mulch to breakdown more quickly. Many growers rototill or disk the mulch at the end of the season. Using an interseeded can be a problem when planting a fall cover crop with mulch present. Pieces of mulch can be entangled in the seeder or even a rototiller.

A farm in the western US was able to supply their CSA members with a much wider selection of crops this year while using biodegradable mulch. The farm is located in La Jara, Colorado where the growing season is about 90 days (8000’ elevation). By using biodegradable mulch, they have added 2-3 weeks to their season. Eggplant, cucumbers and peppers are now grown. Overall farmers are very happy with the mulch’s performance on their farm. They feel biodegradable mulch has many advantages despite its high cost. They don’t have the cost of dumping fees and labor to remove it or plastic in their fields.

Important Tips for Success with Biodegradable Mulches

Storage

Cool and dry- this product will start to degrade if stored warm and moist!
Buy what needed each year
Store upright, on ends avoids getting holes in the roll

Application

Do not stretch as tight as standard black plastic
- Stretching starts the degradation
- Will increase rate of breakdown

Apply right before planting
- Sunlight and moisture will start breakdown

2007 Commercial Sources

Biobag USA	Dubois Agrinovation
www.biobagusa.com	www.DuboisAg.com
1-800-959-2247 1-800-959-2248	1-800-667-6279

Preliminary Trials in Organic Vineyard with Mater-Bi® Mulch Films

Guerrini, S.[1], Martellucci, R.[2], Nardi, G.[3], Ranghino, F.[1], & Bonanzinga, M.[4]

Keywords: biodegradable mulch film, weed control

Abstract

Weed control in organic vineyards requires several manual operations, mainly in the first two years after transplanting, and it represents an important cost for the grower. Therefore, mulching can be an interesting practice in order to reduce work on weed control on the rows, increase vine growth, and protect soil from erosion. In this study, biodegradable films were used. The films are made of Mater-Bi®, Mater-Bi, a certified biodegradable and compostable plastic that contains vegetable raw materials such as GMO-free cornstarch modified with biodegradable polyesters. Thanks to their biodegradation, mulch films do not need to be removed from the soil as do traditional plastics.

In the last couple of years some experiences in different vineyards in Tuscany have been carried on by ARSIA using black Mater-Bi films with different thicknesses and different formulations. The preliminary quantitative results were collected from the experimental trial in the organic vineyard "Il Poderaccio" near Siena. Biodegradable mulch films were laid by hand on one row after vine transplanting in spring and the behavior of mulched and not mulched vines (an adjacent row) was compared.

Recurring monitoring has shown that some biodegradable mulch films were able to reduce the growth of weeds for a period of 12 months. Film thickness and formulation play an important role in the efficiency of long-lasting biodegradable mulch films.

Already at the budding stage and until the end of the vegetative cycle, the development of mulched vines has been higher compared to vines without mulching. Causes of this greater growth can be a result of a faster soil warming in spring (due to the black color of the films), a higher water retention, and a reduction in weed competition.

The studies performed in Tuscany demonstrated that mulching vineyards using biodegradable films can reduce the need for labor to control weeds during the first growing period. However, further investigation will be required in order to obtain more data to confirm this initial result.

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Use of biodegradable mulching in vegetable production

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Keywords: soil mulching, thermoplastic starch, implementation, BIOMASS project.

Abstract

Trials were carried out in Liguria during three years (2004-2006) to evaluate the use of innovative starch based bioplastics for soil mulching. All trials carried out in open field as well as in greenhouse on different vegetable crops demonstrated the effectiveness of biodegradable films in controlling weeds and in increasing yield. The use of biodegradable mulching films found application in integrated production regulations set up by the regional authority and it is potentially adoptable in an organic farming context.

Introduction

Biodegradable mulching films represent a good alternative to herbicides or other chemicals for soil disinfestation, particularly when used just for weed control, being especially useful in organic farming (Minuto *et al*., 2002). Mater-Bi materials, produced by the Italian company Novamont Spa, have been introduced for several applications due to their different available processing systems, mechanical and physical properties and permeability to water. Mater-Bi materials are biodegradable, according to the European standards (Bastioli, 1997, 1998) and they can be industrially processed and produced by means of traditional film blowing and casting equipment (Thunwall *et al*., 2007). They have been adopted in the framework of demonstrative activities promoted by the European project LIFE04 ENV/IT/463 “BIOMASS” focused on the promotion of the substitution of existing non-biodegradable polymers with new biodegradable starched based plastics.

Materials and methods

Trials were carried out both in greenhouse and in open field in Liguria (La Spezia and Albenga locations); trial locations in La Spezia are certified for organic production. The behaviour of Mater-Bi films (NF 803/P - 12, 15 and 18 μm thickness) were compared to non biodegradable black polyethylene film (PE) (40 μm thickness). All films were laid both manually and mechanically and tested at least three times on different crops. The crops were managed following the cultural techniques commonly adopted by growers. Water was distributed through drip irrigation system. A complete randomised block design with 3 or 4 replicates of 25 m^2 to 300 m^2 each was applied. Data regarding behaviour of films during the crop cycle, mulching effect, crop yield, degree of degradation in the soil and climate condition were collected. In all demonstrative

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and experimental plots the effects of mulching films were evaluated counting the number of weeds/m^2 and, in some cases, the fresh weight (g/m^2) of aerial parts. The quantity (g/m^2) of biodegradable film on the surface of the soil and in the soil was evaluated 14 days after rototilling. All data were statistically analysed using Duncan's multiple range test (P=0.05). A comparison between costs of PE and biodegradable films was also calculated.

Results

Main results about trials carried out on tomato, lettuce, zucchini and Brussels sprouts are presented. Good results in terms of weed control and % of soil covered were obtained with 12 and 15 μm thick films designed for short crop cycles (from 3 to 5 months) (Table 1 and 2).

Tab. 1. Percentage of mulched soil, degradation of mulching film and effect on weeds of biodegradable and PE films on tomato^ crop grown under plastic tunnel [Sarzana (SP), March – September 2006].

Mulching film – thickness (μm)	% of mulched soil at						Degradation index of film at the end of the crop				Weeds at the end of the crop			
	25/04		02/07		12/09		film upon the soil °		buried film °°		number/m^2		Kg/m^2	
NF 803/P – 12	100	a*	90	a	85	a	7.3	b	3.6	c	3.0	a	0.4	a
NF 803/P – 15	100	a	90	a	85	a	8.4	a	6.6	b	0.9	a	0.2	a
PE black – 50	100	a	100	a	100	a	9.0	a	9.0	a	0.0	a	0.0	a
Bare soil	-		-		-		-		-		39.0	b	5.4	b

^Randomized blocks with 3 replications; Cultivar of tomato: "Pera d'Abruzzo"; density of cultivation: 6 plants/m^2; mulched surface/plot: 300 m^2; water supply: drip irrigation; film drawing up: mechanized; soil texture: silt (>90%); soil pH: 7.0. * Values followed by the same letter do not significantly differ according to Duncan's multiple range test (P=0.05). ° Degradation index of the film upon the soil (1=0% of mulched soil till 9=100% of mulched soil) and of the buried film (°°).

Tab. 2: Efficacy of different mulching films on tomato, zucchini and lettuce^ yield at the end of growing cycle [Sarzana (SP), March – November 2006].

Mulching film – thickness (μm)	Tomato °				Zucchini °°		Lettuce °°	
	Kg/plant		N° fruits/ plant		Kg/plant		Kg/m^2	
NF 803/P – 12	4.2	a*	13.3	a	4.5	a	278.0	a
NF 803/P – 15	4.8	a	14.2	a	4.6	a	296.6	a
PE black – 50	4.7	a	13.7	a	4.3	a	310.0	a
Bare soil	2.9	b	12.7	b	2.1	b	78.0	b

^Randomized blocks with 3 replications; mulched surface/plot: 300 m^2; water supply: drip irrigation; film drawing up: mechanized; soil structure: silt (>90%); soil pH: 7.0. *See table 1. ° Plastic tunnel, Cultivar "Pera d'Abruzzo", 6 plants/m^2 (march-september, 2006); °° Open field, Cultivar "Ibis", 2 plants/m^2 (may-august, 2006); °°° Plastic tunnel, Cultivar "Lollo verde", 20 plants/m^2 (September-november, 2006).

During the growing cycle only a limited degradation was observed, with tears and visible degradation particularly located in the buried parts. The residues of biodegradable film observed on the soil surface (g/m^2) immediately before rototilling, compared with the weight of new films, indicated that the degradation process of the material was already started. The same evaluation carried out 14 days after rototilling sieving the soil up to 20 cm depth confirmed the almost complete degradation of the film (Table 3).

Tab. 3: Film residues at the end of crop cycle of some vegetable crops (open field, winter-spring, Albenga 2005).

Mulching film –	New film	Tomato				Brussels sprouts				Lettuce			
thickness (μm)	(g/m²)	residues of film at the end of the crop cycle (g/m²)											
		upon soil°		in the soil^		upon soil°		in the soil^		upon soil°		in the soil^	
NF803 – 18	25.0	8.3	b*	0.6	b	4.0	b	2.2	b	7.8	a	0.9	b
NF803 – 15	22.9	7.4	a	0.4	a	2.2	a	1.2	b	7.0	a	0.7	b
NF803 – 12	15.3	7.2	a	0.2	a	1.3	a	0.1	a	7.0	a	0.2	a
PE black – 50	n.a.**	n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-	n.a.	-
Bare soil		-	-	-	-	-	-	-	-	-	-	-	-

° g/m² of film residues upon soil before rototilling; ^ g/m² of film residues in the soil (evaluated sieving the soil up to 20 cm depth) 14 days after rototilling; * see table 1; ** because of technical and environmental reasons PE was not incorporated in the soil.

Tab. 4: Comparison between the costs of biodegradable films and conventional PE (being equal the application costs).

Characteristic of the film	PE	Mater-Bi films	
Thickness (μm)	45	15	12
average weight (Kg/ha)	450	180	140
Cost of the product (€/ha)	639	900	700
Cost difference (€/ha) (base: PE)	-	261	61
Cost difference (%) (base: PE)	-	40,85	9,55
Average removal cost (€/ha)	120	0	0
Average disposal cost (€/ha)	50	0	0
Overall cost of the product (€/ha)	809	900	700
Overall cost difference (%) (base: PE)	-	11,25	-12,11

Crop yield was not influenced by the different thickness of the mulching films and significantly differed from the yield obtained on bare soil due to high weed competition (Table 2). No differences in terms of film behaviour were observed between manually or mechanically laid films. Costs of biodegradable films (12 and 15 μm thick) including product, removal and disposal costs, proved to be comparable with the ones of conventional PE (Table 4).

Discussion

The results obtained testing different formulations of biodegradable films were generally encouraging and similar to those achieved by normal black PE. The same film behaviour was observed even on other crops which were grown during trials such as artichoke, garlic, onion, sweet pepper, water melon, eggplant and strawberry (data not shown). Thanks to their characteristics biodegradable films could mulch almost completely the soil during the crop cycle as well as standard PE assuring a constant control towards weeds and maintaining an accurate level of moisture in the soil. During application, mechanically laid films must be let free to rotate without any brakes in order to avoid stretching and consequent film thinning. No particular concerns are related to manual application. Biodegradable films proved also to be able to increase crop yield and quality and they are worth being used at the same extent of traditional films in consideration of the fact that even their cost is comparable when costs related to plants, removal and disposal of traditional films are taken in consideration. The evaluation of the percentage of mulched soil at the end of the crop along with crop yield suggests that an efficient weed control can be achieved as long as the film totally covers the soil during the major part of the crop cycle.

Conclusions

The major concern on biodegradable films in agriculture is primarily due to the effects of ageing and degradation during the growing cycle for long lasting applications, when premature breakings of the films can limit their applications. At this regards other researches demonstrated that well produced biodegradable films perform in a way comparable to the corresponding PE films (Briassoulis, 2007). Results demonstrated the effectiveness of biodegradable films manufactured using Mater-Bi films against weeds. Tested films appeared to be easily adapted during different seasons, in open field and under greenhouse conditions, being able to substitute conventional PE films for short crop duration. The revision of integrated production protocols and a further implementations of regulations at a regional level is expected to enhance a wider adoption of biodegradable films for the control of weeds without resorting chemical inputs, so stressing their capability to be used even for organic production.

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Product Development Research Report

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The Effectiveness of Biodegradable Poly(Hydroxy Butanoic Acid) Copolymers in Agricultural Mulch Film Applications

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Abstract

The ability of poly(hydroxy butanoic acid) or PHB copolymers to degrade microbially in soil makes them ideal for agricultural mulch film applications. This report summarizes preliminary observations regarding crop growth response, in open-field and high-tunnel environments, using PHB copolymer mulch films with comparisons to polyethylene mulch films. The biodegradation kinetics of the subject films and the molecular architectural factors that influence it, after they are ploughed into the soil, is discussed. Finally, the social, environmental and economic benefits of using biodegradable mulch films are outlined.

Conclusions & Recommendations

PHB copolymers are very well suited for agricultural mulch film applications. Vegetable crop growth performance with PHB copolymer mulch films, from open-field and high-tunnel environments, is considerably better than bare-ground crop growth and similar to crop growth with polyethylene mulch films.

PHB copolymers are known to readily disintegrate through microbial action even at ambient temperatures. The subject films were shown to biodegrade in soil, with complete breakdown anticipated in months depending on soil make-up, soil temperature and film composition. The mulch films were ploughed into the soil after crop harvest; this eliminates the environmental and social concerns regarding mulch film retrieval and disposal. Because incineration and landfill disposal are the most commonly employed means of eliminating the incumbent polyethylene mulch films, natural biodegradation of the ploughed-in film is not only an eco-friendly alternate but it is also a considerably more efficient farming practice.

In addition to the advantages of biodegradation at ambient conditions, the use of *Mirel*™ PHB copolymers exerts a considerably lesser strain on the environment as it is based largely on renewable resources (corn sugar) as opposed to petroleum-based polyethylene. Further, an independent life cycle analysis of *Mirel*^{TM} PHB copolymer production indicates a 95% reduction in the use of non-renewable energy and a 200% reduction in greenhouse gas emission compared to the production of conventional petroleum-based plastics.

The influence of certain molecular architectural attributes on the soil degradation behavior of PHB copolymer films was also investigated. These experiments indicated that high molecular weight and high crystallinity hinder the rate of degradation in soil. Further, the soil degradation kinetics was found to be insensitive to the presence of long chain branching (introduced through reactive extrusion with low levels of an organic peroxide) in the polymer.

The soil degradation kinetics of PHB copolymer films can be considerably delayed by using multi-layered co-extruded films with higher crystallinity and/or higher molecular weight compositions on the skin layers.

The black mulch films employed in this investigation did not have adequate tensile strength, tensile extensibility and tear resistance. This not only made the use of the standard mulch film applicators challenging, but also caused some sections of film to tear during the crop growth cycle. The less-than-adequate film properties were attributed to low molecular weight and poor carbon black dispersion. These issues need to be addressed to ensure commercial success in this application; this calls for a greater understanding of the extrusion characteristics of our polymers including developing guidelines for appropriate screw design.

There were some signs of microbial degradation of the film during the early stages of the crop growth cycle; this was particularly pronounced in areas where the film made intimate contact with the soil. It is desirable to delay the onset of soil degradation of *Mirel*^{TM} mulch films such that they may be employed robustly in a variety of climatic conditions. The identification and utilization of appropriate anti-microbial additives is therefore important.

Background on Mulch Films

Plastic films were first used in agriculture in 1948 when Prof. Emmert (University of Kentucky) created a glasshouse using cellulose acetate film instead of the more expensive glass (1). The cellulose acetate film was subsequently replaced by low-density polyethylene (LDPE) film. The large-scale production and availability of LDPE in the 1950s led to the creation of a new discipline, *plasticulture*, which deals with the use of plastics in agriculture. Mulch films, drip irrigation tubing and row covers were some of the first applications for plastics in agriculture (2, 3).

Plastic films have allowed previously unproductive desert areas, such as in the province of Almeria (Spain), to become models of agricultural development (3). Close to 100 million lbs of PE mulch film is consumed every year in the USA, while a considerably larger amount of such films are employed in China, Europe and Asia Pacific. Mulch films are films placed directly over the soil/ground during the initial stages of plant growth. Plastic mulches directly influence the microclimate around the plant by altering the radiation budget (absorbtivity versus reflectivity) of the soil surface and by minimizing water loss from the soil (4, 5). The advantages of using mulch film for crop growth, as opposed to the bare ground approach, are increased yields, earlier-maturing crops, higher-quality crops, enhanced pest management and weed control (2). Mulch films also allow other plasticulture systems to achieve maximum efficiency.

Polyethylene (PE) films are the predominant films used in mulching. Mulch films can be black, translucent, white, co-extruded white on black, or colored. Black films are good at absorbing solar radiation (UV, visible and IR wavelengths), but they are poor transmitters; they can help enhance soil temperature by 2-4 °C (at a 2-inch depth) when the soil-film contact is good and continuous (2). Black films are also very good at weed control. Clear/translucent films are poor absorbers but good transmitters. The underside of clear films usually has a covering of condensed water droplets that are opaque to the outgoing long-wavelength IR radiation; consequently, the soil temperature with clear mulch films is enhanced by 4-10 °C. However, clear films are not very good at weed control. White and reflective mulch films are used in regions where it is necessary to lower soil temperature as they reflect back most of the incoming solar radiation. Certain wavelength-selective mulch films contain moieties/additives that selectively absorb photosynthetically active radiation and transmit solar infrared radiation thereby achieving a compromise between black and clear mulch films; these films offer the weed control properties of black mulch films with soil temperature enhancement that is intermediate between black and clear films (6).

Mulch films are typically employed during the early stages of crop growth and are left on the ground for up to an entire growth cycle. The disposal of mulch films, after crop harvest, has been and will continue to be a considerable concern. Because these films have entrapped dirt, soil, plant debris and moisture, it is highly impractical and extremely expensive to render them suitable for recycling. Incineration of the films has drawbacks as well, because of the potential of releasing toxic fumes to the atmosphere. Another option is to dump used mulch films in landfill sites. While landfill disposal and incineration are commonly employed to dispose used mulch film (and other plasticulture products), these methods are neither socially nor environmentally acceptable. In fact, the United States Environmental Protection Agency (EPA) hierarchy of solid waste management (based on energy consumption, resource value, environmental damage and other factors) consider waste combustion and landfill disposal options to be less desirable compared to source reduction and composting. Lastly, incineration and landfill disposal options are not inexpensive and consequently impose a financial strain on farmers.

Advances in polymer and additive technology have allowed mulch film producers to use thinner PE films to minimize some of the above concerns; however, this approach is clearly not an adequate long-term solution. Photodegradable mulch films (PE films with additives that enable them to be broken down by ultraviolet sunlight) have also been employed with limited success, largely because of their inability to breakdown completely and also because of the scattering of film fragments by wind (7). Biodegradable polymers are an extremely attractive option for mulch film applications, particularly if the films can be ploughed into the soil for biodegradation after crop harvest. In this report, we will discuss the effectiveness and the value proposition offered by one class of biodegradable polymers, namely poly(hydroxybutanoic acid) or PHB copolymers for agricultural mulch applications.

Background on PHB Copolymers

A remarkable discovery, dating back to 1926, documents the presence of thermoplastic polyesters within bacterial cells (8, 9). The basic polyester that Lemoigne isolated and characterized was poly (3-hydroxybutanoic acid) or P(3HB). This discovery is of particular significance because it preceded the recognition of polymeric or macromolecular architectures first by Herman Staudinger and later by Wallace Carothers. It was later determined that the P(3HB) granules within the bacterial cells serve as an intracellular food and energy source and are produced in response to a nutrient limitation in their immediate vicinity so as to prevent starvation during times of scarcity (10, 11). P(3HB) is an ideal carbon storage medium because it is inert to water, chemicals and osmosis, and can be readily converted to monomeric form by a series of enzymatic reactions (12-14).

Bacterial polyesters became commercially significant when ICI (Imperial Chemical Industries) started producing a PHB copolymer under the trade name “Biopol”. Other corporations, most notably W. R. Grace Company, also invested considerable effort looking into the possibility of producing such polymers on a commercial scale. These initial efforts were abandoned possibly due to the high investment required for commercial-scale fermentation and product recovery (13). Recent discoveries (15-19) in genetic engineering led to the creation of a new company, Metabolix. In 2006, Metabolix formed a 50-50 joint venture with Archer Daniels Midland (ADM) to commercialize the production of PHB copolymers under the trade name *Mirel*™. The polymers are made by microbial fermentation of sugars such as corn sugar or cane sugar or vegetable oils. Copolymers of PHB are produced during the fermentation step by introducing a suitable comonomer feed (14). Because P(3HB) is stored by bacteria for eventual breakdown and consumption, these polyesters are biodegradable in a variety of environments wherein the macromolecule is hydrolyzed enzymatically to monomeric form. Although the basic polymer stored as intracellular food source is the P(3HB) homopolymer, the following PHB copolymers are known to undergo microbial degradation: 3HB-4HB copolymers, HB-HV copolymers where HV stands for hydroxyvalerate and HB-HX copolymers where HX stands for hexanoate (14).

Mirel^{TM} polymers (3HB-4HB copolymers) and their products are known to biodegrade in soil, home compost, and industrial compost sites; they also biodegrade in fresh water and sea water environments. Because of their ability to biodegrade in soil, PHB copolymer films (blown and cast) may be ideally suited for agricultural mulch applications. In this study, we report on the potential and advantages of PHB copolymer mulch films, with a focus on vegetable crops.

Experimental Section

Film Processing

PHB copolymer films (monolayer, cast) for the mulch studies were made at the **Alcan Packaging Research Center** using a 89 mm 28:1 Egan extruder fitted with a 137 cm single manifold cast film die (coat-hanger design). The extruder, which was fitted with a barrier screw with a Maddock mixing head, was operated at about 25 rpm to yield an output rate of about 484 kg/hr. The melt temperature was about 180 °C, while the extrusion pressure was about 3650 psi. The primary and stripper rolls on the cast film take-up assembly were heated to about 50 °C, and the line-speed was adjusted to produce films that were about 75 microns (3 mils) and about 50 microns (2 mils) in thickness. The films produced for the crop growth studies were black; carbon black was introduced through a masterbatch approach whereby the masterbatch pellets were physically mixed with the virgin pellets just prior to the introduction of this mixture into the extruder hopper.

Cast films for the soil degradation experiments were produced using a 19 mm RandCastle extruder equipped with a standard compression screw with a recirculating element. A 25 mm cast die was used to produce the films. The extruder was operated at 80 rpm to yield an output rate of about 1.7 kg/hr. The melt temperature was about 175 °C, while the extrusion pressure was about 3400 psi. The cast film rolls were heated to about 60 °C during the run. These films did not contain any carbon black. Three-layer (A/B/A) co-extruded films were also produced during this run; polymer for the 'B' layer came from the 19 mm extruder listed above, while the polymer for the 'A' skin layers came from a 25 mm extruder running at about 22 rpm. The net output rate for the co-extrusion runs was about 3.3 kg/hr, resulting in a A/B/A composition of about 25/50/25 (on a weight basis).

Crop Growth

Various vegetable crops were grown using the 50 micron (2 mils) thick and the 75 micron (3 mils) thick black PHB copolymer mulch films. These studies were carried out at the Horticulture farms in Pennsylvania State University. Two control experiments were also included in the experimental plan: they were a bare-ground control and a black PE mulch film control (Nolt's Produce Supplies 3' raised bed/mulch). These crop growth experiments were performed in an open field as well as in a high-tunnel. Black PE drip irrigation tubes (Toro Ag 0.45 gpa/100 ft. tape – 8 mil, 12 orifice spacing) were used as the primary water source for all the crop growth experiments; the open field experiments did receive additional water from rainfall. All of the crop growth experiments were performed in a randomized complete block fashion with 3 replicates.

The following fertilizer application protocol was followed for both open-field and high-tunnel experiments: 128 kg/A-N, 240 kg/A-P and 240 kg/A-K broadcast incorporated prior to making raised beds. All plants were fertigated with 20-10-20 (11.2 kg/A). No herbicides were used; hand weeding and cultivating between rows were employed.

For the open field experiments, Zucchini Squash (Payroll) and Bell Pepper (King Arthur) were grown on a plot 7.3 m long and 46 cm wide using a raised bed. The plant spacing was 61 cm in-the-row between plants and 244 cm between rows. The crops were planted on July 10th, 2007; the zucchini squash was harvested between August 17th and September 19th, while the bell peppers were harvested between September 12th and October 12th.

For the high-tunnel experiments, Patty Pan Squash (Sunburst) was grown on a plot 7.3 m long and 46 inches wide using a raised bed. The plant spacing was 91 cm in-the-row between plants and 1.2 m between rows. The crops were planted on August 10th, 2007 and harvested between September 23rd and October 25th.

Results and Discussion

Crop Growth

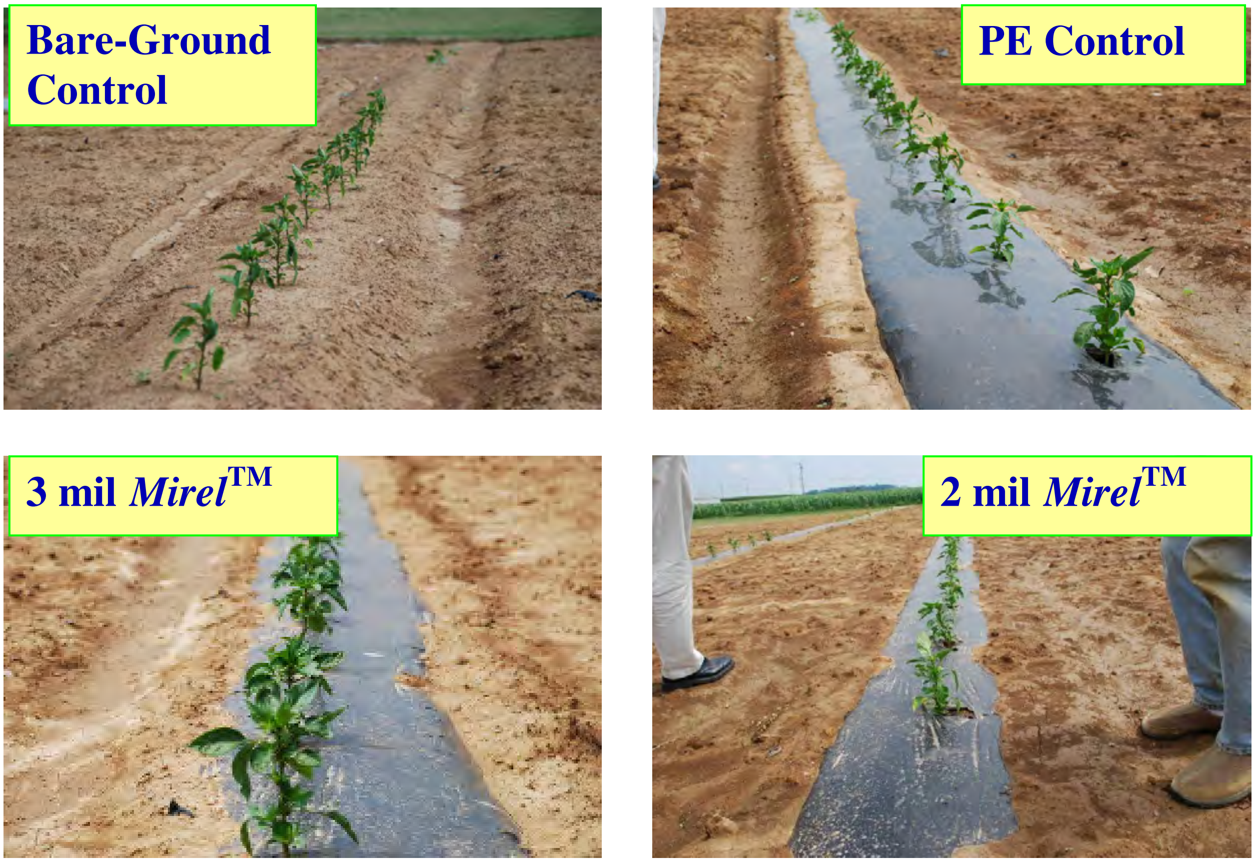

Figure-1: Pictures of the Penn State Horticulture Farm showing the open-field crop growth experiments.

Figure 1 shows the Penn State horticulture farms with the bell pepper open-field experiments during the early stages of crop growth. This set is one of the three replicates studied.

Figure 2 shows the crop yield data for zucchini grown in the open field; data for the bare ground control, PE mulch film control and the PHB copolymer mulch films are included in the charts. The data of interest are the number of fruit harvested, the total mass of fruit harvested and the mass per fruit harvested. Compared to the bare-ground control, the crop yield for those grown using any mulch film is considerably higher. This is not a surprising result and is consistent with the documented benefits of using mulch film. Interestingly, the crop yield results (both number of fruit harvested and the mass of each harvested fruit) for the biodegradable PHB copolymer films are similar to that of the PE mulch film.

Figure 2: Zucchini squash crop yield data for the open-field experiments.

Figure 3 shows the crop yield data for the bell pepper plants grown in the open field. Compared to the bare-ground control, the crop yield for those grown using any mulch film is considerably higher. The plants grown in bare-ground were smaller and slightly yellow in appearance compared to the others throughout the growing season. While the number of fruit harvested from the PE mulch film control were slightly higher than that of the PHB copolymer films, the mass (or health) of each fruit harvested from the PHB copolymer films was slightly higher.

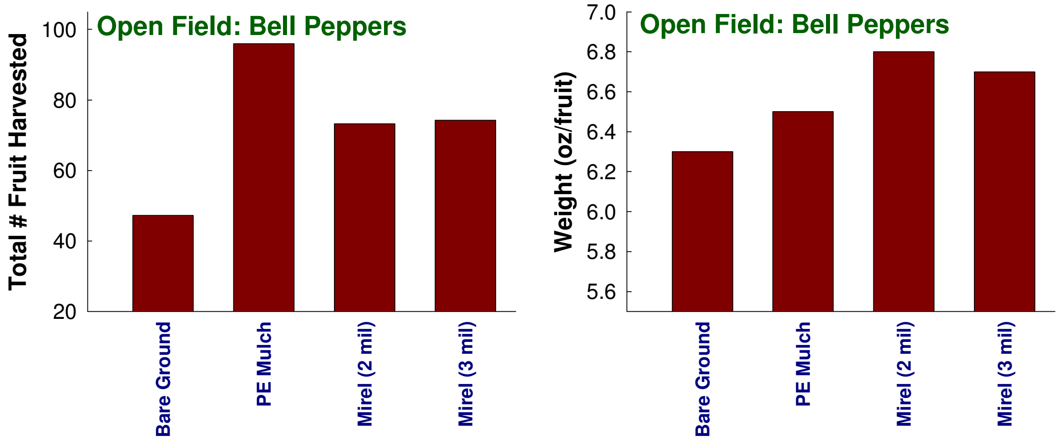

Figure 3: Bell pepper crop yield data for the open-field experiments.

Crops grown inside high-tunnels are generally protected from the elements compared to those grown in open fields. Figure 4 shows the crop yield data for zucchini plants grown in a high-tunnel; data for the bare ground control, PE mulch film control and the PHB copolymer mulch films are included in the charts. Compared to the bare-ground control, the crop yield for those grown using any mulch film is considerably higher. The number of fruit harvested from the

PHB copolymer mulch films is considerably higher than that of the PE mulch film control while the mass (or health) of each fruit harvested from the PHB copolymer and the PE films was similar. The difference in performance (total number of fruits harvested), between the biodegradable mulch film and the PE mulch film, may be partially attributed to the difference in soil temperature; the bed on which the PE mulch film was laid was closer to the edge of the high-tunnel, while the bed on which the biodegradable mulch film was employed was closer to the middle of the high-tunnel.

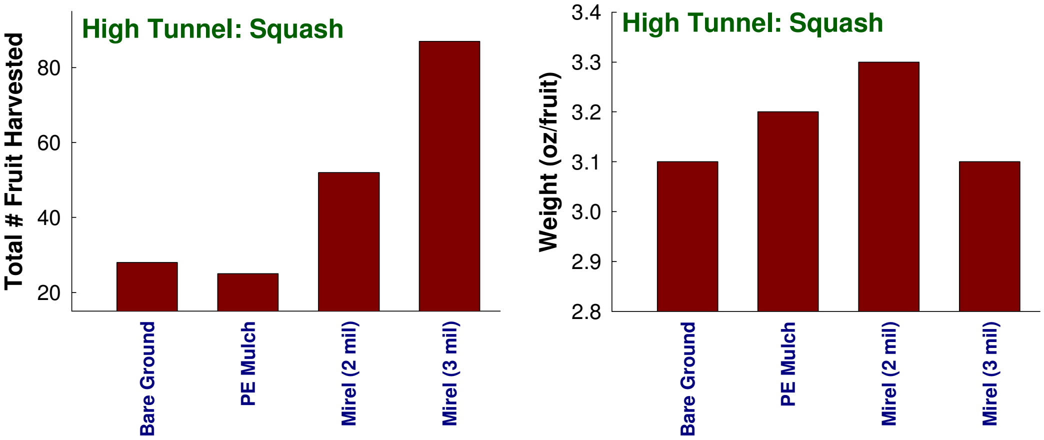

Figure 4: Patty pan squash crop yield data for the high-tunnel experiments.

After harvesting the last of the crops in October, the non-degradable mulch film was retrieved from the field for subsequent disposal (landfill site). However, the biodegradable PHB copolymer mulch films were ploughed into the soil for biodegradation. This approach eliminates the time, effort, costs and environmental concerns regarding the retrieval and disposal of the PE mulch films. The soil will be checked in the spring of 2008 for any mulch film residue. A soil assay will also be performed on this soil sample to test for any undesirable biodegradation residue.

Soil Degradation

One of the attractive attributes of the subject PHB copolymers is their ability to biodegrade in soil at ambient temperatures. Various microorganisms that are present in the soil excrete extracellular depolymerases that enzymatically degrade PHB copolymers and the resulting products (dimers, monomers) are consumed as nutrients. In fact, a variety of microorganisms are known to flourish with P(3HB) as their solitary carbon source (20-22). Even though P(3HB) homopolymer is the default reserve food source stored in the bacterial cells, various copolymers of PHB are known to degrade microbially (23). Doi and co-workers have carried out enzymatic degradation studies on PHB copolymer films under highly controlled conditions (14, 23). These studies indicate that degradation proceeds through a surface erosion mechanism, whereby the enzymes hydrolyze the polymer chains that are most readily exposed while the remainder of the chains in the bulk of the film is intact. These specific enzymes also seem to consume copolymers of P(3HB) and P(4HB) much more readily compared to P(3HB) homopolymers (14, 23).

Besides the enzymatic degradation, PHB copolymers can also undergo simple hydrolytic breakdown at slightly above-ambient temperatures. This occurs in two stages: random chain scission during the initial stages (lowering of molecular weight without any noticeable weight loss) and the onset of subsequent weight loss after the attainment of a critical molecular weight. The rate of hydrolytic breakdown is thought to be considerably slower than that of microbial degradation at typical soil temperatures (14).

The soil degradation experiments carried out in this investigation probably encompass a combination of enzymatic degradation and hydrolytic breakdown of the polyester chains. For these studies, small pieces of film (~ 5 cm by 9 cm) were buried (last week of July'07) in the soil and retrieved on a weekly basis (for 16 weeks, starting from the 4th week); the mass of the retrieved film specimen was compared to the original film mass, with the percent loss in mass giving an indication of the extent of degradation. Molecular weight, crystallinity and peroxide-induced branching were the molecular architectural variables studied. Crystallinity of the PHB was varied by changing the copolymer composition. The various films that were investigated are described in the table below:

Sample ID	**Composition**	**Film M_w** (kg/mol)	**Weight % Crystallinity**
A	M3640	385	26
B	M3640	343	26
C	M3640	295	26
D	Skin/Core/Skin 20/60/20 Co-Ex Film Skin: M6000 Core: M3640	370	31
E	M3640/M6000 70/30 Blend	382	30
F	M3640/M2000 70/30 Blend	380	23
H	M3640 with 0.1 wt% peroxide	395	25
I	M3640	495	26

All of the above films had about 5 weight percent of a slip/anti-block masterbatch (from Ampacet) and about 5 weight percent Citroflex A4 plasticizer blended in.

In Figure 5, the weight loss trends of four films (C, B, A and I) that are similar in composition and total crystallinity but differ considerably in their initial molecular weight are shown. A clear molecular weight dependence is evident, with higher molecular weight films showing considerably slower degradation. Film 'C' (lowest molecular weight) was almost completely degraded in four weeks, when the first sample was retrieved. Film 'B', which is slightly higher in molecular weight relative to 'C' starts to degrade a bit slower and is almost completely gone in about 8 weeks. Films 'A' and 'I' degrade much more slowly compared to 'B' and 'C' with 'A' beginning to be completely degraded in about 16 weeks. For 'I', only about 20% of the initial mass was lost to soil degradation after 16 weeks. The molecular weight of the partially degraded films was measured and noted to be very similar to that of the original as-made film. Consequently, if there is any change in sample mass that accompanies some random chain scission processes (such as in conventional hydrolytic breakdown at high temperatures), we have been unable to capture that.

Doi's research suggests that molecular weight is not an important contributor to enzymatic degradation, while it is a very important consideration for hydrolytic breakdown (14). However, we were unable to capture any change in the molecular weight of the film during the soil degradation process; this suggests that hydrolytic breakdown of the macromolecules is not significant under the imposed test conditions. Further, while Doi's enzymatic degradation studies were limited to enzymes from specific bacteria, it is very likely that the subject films are exposed to a variety of bacteria and fungi in the soil and that their collective response is sensitive to molecular weight.

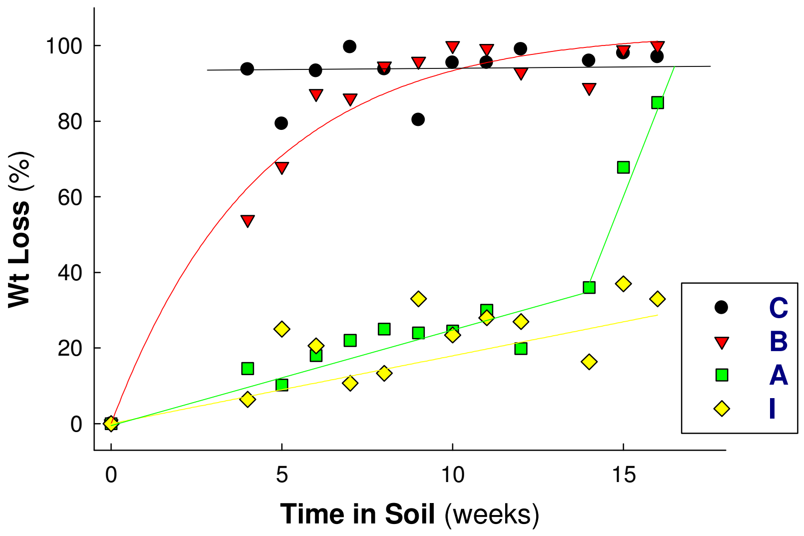

Figure 5: Weight loss (in soil) trends for films C, B, A and I that differ in molecular weight. The data points are actual measurements while the colored lines are included as guides only.

Films 'E' and 'F' are similar in molecular weight, but they differ considerably in crystallinity. Their weight loss trends over time are shown in Figure 6. Comparing the results for 'E' and 'F', it is clear that higher crystallinity results in slower soil degradation kinetics. In other words, the higher mobility of the chain segments in the non-crystalline regions render them to be more suitable for microbial attack; this is not surprising given that the P(3HB) stored within the bacterial cells is wholly-amorphous while purified P(3HB) is highly crystalline.

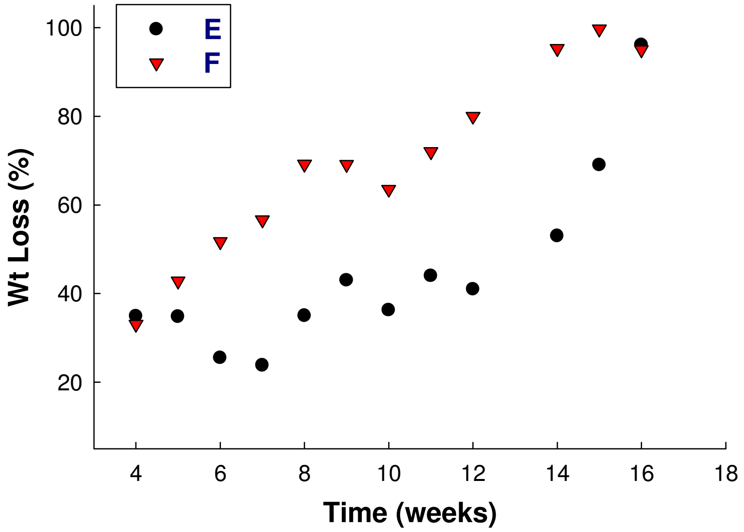

Figure 6: Weight loss (in soil) trends for films E and F that differ in crystallinity. The data points are actual measurements.

All of the soil degradation results we have discussed thus far have been based on experiments performed on mono-layer films and we understand that both molecular weight and crystallinity are important considerations. In this section, we shall discuss the performance of three-layered, co-extruded films. Specifically, we will evaluate the performance of a 3-layer film ('D') with the skin layers composed of a higher crystallinity PHB copolymer composition.

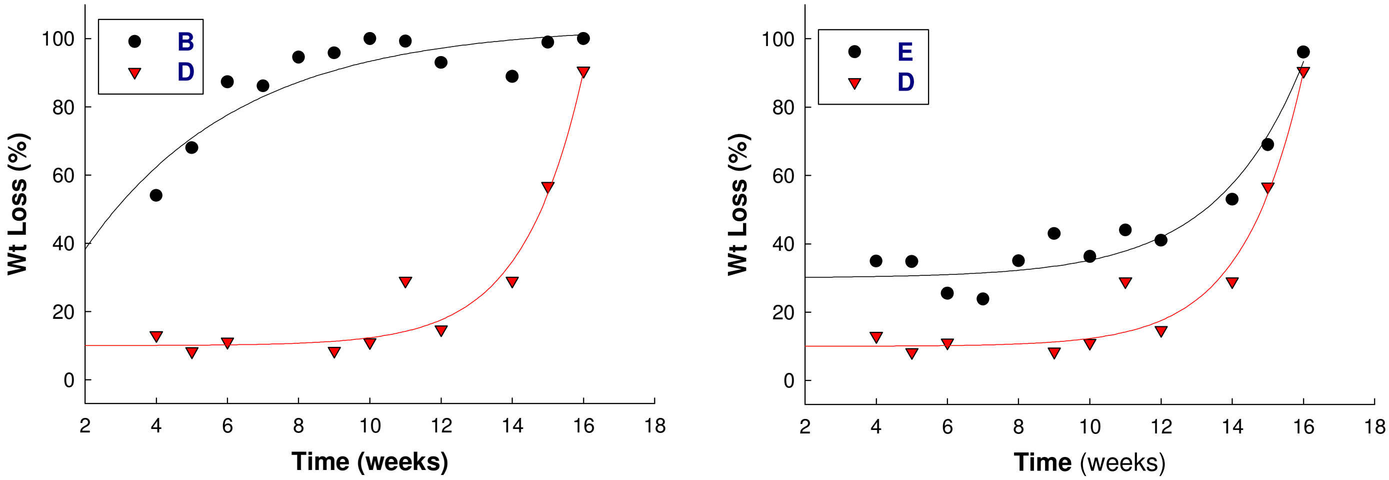

Figure 7: Weight loss (in soil) trends comparing mono-layer films to multi-layer co-extruded films with high crystallinity skin layers. (A) 'B' Vs. 'D'; (B) 'E' Vs. 'D'. The data points are actual measurements while the colored lines are included as guides only.

The soil degradation behavior of the co-extruded film (relative to other monolayer films) is shown in Figure 7. The inner core portion of 'D' has the same polymer composition and molecular weight as that of 'B' monolayer film. From Figure 7A, 'B' is noted to degrade much faster compared to 'D'. In fact, it appears like the presence of the high crystallinity skin layer is providing an incubation time or causing a delay in the onset of degradation. However, because of the higher crystallinity skin layers that account for about 40 weight percent of the entire film, the overall crystallinity of 'D' is higher than that of 'B'.

Films 'E' and 'D' are similar in overall crystallinity and molecular weight. The outer skin layers in 'D' are higher in crystallinity relative to its inner core; however, the total crystallinity of 'D' is similar to that of 'E'. Figure 7B compares the weight loss trends of 'D' and 'E'. The considerably slower overall degradation of 'D' (relative to 'E') can be attributed to the higher crystallinity skin layers protecting the lower crystallinity core layers from enzymatic attack until its consumption. While this observation confirms the generally expected surface erosion mechanism of microbial degradation, it also offers us an avenue to tailor the degradation characteristics of mulch films.

In Figure 8, the soil degradation kinetics of 'A' and 'H' are compared. The polymer used to make film 'H' is essentially the same as that of 'A' with the exception of low levels of an organic peroxide (0.1 weight percent) blended-in during extrusion to facilitate the creation of low levels of rheologically significant long branches; this reactive extrusion approach helps increase polymer melt strength considerably. From Figure 8, we conclude that such an architectural modification attained through reactive extrusion of PHB with low levels of a suitable peroxide does not change the inherent soil degradation behavior of the resulting film.

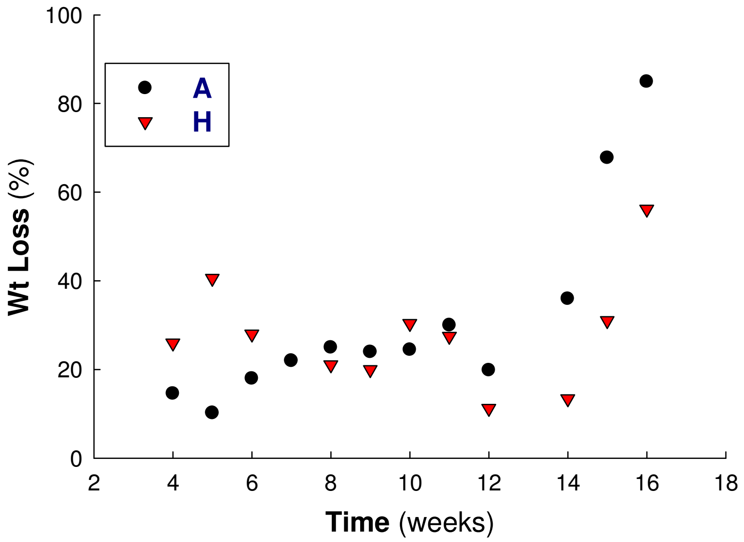

Figure 8: Weight loss (in soil) trends for films 'A' and 'H' that are similar in molecular weight and crystallinity. 'H' contains peroxide-induced branching while 'A' does not. The data points are actual measurements.

Film Characteristics

While the crop growth response from the PHB copolymer mulch films used in this study was excellent and comparable to that of PE films, there were some concerns regarding the mechanical properties of the subject films. Specifically: (i) The films lacked the stretchability and tensile strength required to enable the easy use of automatic mulch film applicators. This resulted in a few tears/splits in the film as they were stretched and placed on the soil. Consequently, there was some undesirable weed growth in certain sections of the raised bed. These mechanical tears propagated over time causing a few film fragments to be lifted off the soil, with a fraction of the fragments tossed around the fields by winds. (ii) The film showed signs of biodegradation as early as two weeks after application; this was particularly noticeable in sections that made intimate contact with soil and moisture. In some portions, the early biodegradation enhanced the propagation of the mechanical tears and splits.

In order to develop a commercially viable solution, the biodegradable mulch films need to have better mechanical properties and a slightly delayed onset of microbial degradation relative to the films used in this investigation. The poor mechanical properties of the films are attributable to: (a) Very poor dispersion of the carbon black particles within the subject mulch films; large chunks of agglomerated carbon black particles are visible to the naked eye. The carbon black dispersion was poor probably because of the rheological mismatch between the base polymer and the masterbatch employed. (b) The molecular weight of the subject films was less than desirable.

While the starting pellets had a weight-average molecular weight ($\boldsymbol{M}_w$) of about 700 kg/mol, the $\boldsymbol{M}_w$ of the resulting film was only about 360 kg/mol. This considerable loss in molecular weight is partially attributable to the less-than-desirable thermal stability of the feedstock. PHB copolymers are well known to undergo chain scission at temperatures very close to its melting point; consequently, the molecular weight change from pellets to product (film, sheet, and so on) is very strongly dependent on the processing characteristics including the extruder and screw type employed. Because the drop in molecular weight is predominantly a thermally-driven process, there is a need to minimize viscous dissipation during extrusion. Therefore, low-compression screws with a higher-than-normal channel depth in the metering section are important considerations during extrusion. However, the extrusion system employed to produce the subject mulch films had a much narrower channel depth and a larger flight clearance than is typical. Specifically, while the generally recommended channel depth is 0.10*Barrel Diameter, this ratio was 0.07 for the production of this film; this increases the viscous dissipation and melt temperature considerably. Also, while the generally recommended flight clearance is 0.001*Barrel Diameter, this ratio was 0.003 for the production of this film; this increases the "leakage flow" and consequently the residence time and viscous dissipation.

While the same pellets used to make the subject mulch films were converted into blown film (without carbon black) on the UMass-Lowell film equipment, the $\boldsymbol{M}_w$ of the resulting film was about 495 kg/mol; this is much higher than that of the mulch film (360 kg/mol). As a result of the different molecular weight and the absence of carbon black, the mechanical properties of the two films are considerably different. The ratio between various tensile, puncture and tear resistance measures of the UMass blown film (termed "UMass Film") to that of the corresponding properties for the mulch film are shown in Figure 9. While the tensile strength of the UMass film are about 25% (MD) to about 140 % (TD) better, the corresponding improvements in the tensile elongation to failure along the MD and TD directions are 400% to 1000%, respectively. The puncture and tear resistance properties of the UMass film are also superior. Consequently, better molecular weight control during film extrusion and better carbon black dispersion are important improvements that need to be incorporated for successful commercialization of this application.

It is also important to be able to delay the onset of microbial degradation of *Mirel*^{TM} films. Therefore, evaluation and implementation of suitable antimicrobial additives is important.

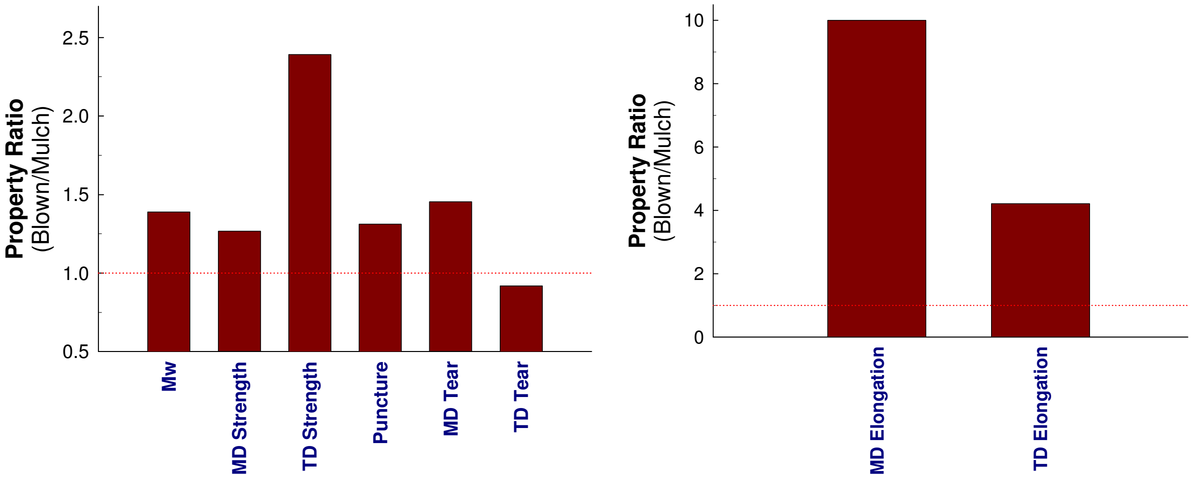

Figure 9: The ratio of various properties of the "UMass" blown film relative to that of the subject mulch film made with the same pellets. The plot on the left show molecular weight, tensile break strength, puncture toughness and tear resistance, while the plot on the right shows tensile elongation. The properties are split into two plots for purposes of scale and clarity.

Economic Considerations

There are some important economic considerations for the use of biodegradable PHB copolymer films, relative to PE films, in mulching applications. Currently, for an acre of cultivated land, it is typical to use about 150 lbs of PE film. This film at about 1.0-1.2 mils thickness will cost about $ 175. The costs associated with the retrieval of the mulch film after crop harvest is estimated to be about $ 120/acre. Finally, the film disposal (landfill) fees are about $ 30/acre. Therefore, for an acre of cultivated land, the film retrieval and disposal costs are almost as much as the material costs. If the PE films are replaced by *Mirel*^{TM} films, they can be ploughed into the soil after crop harvest allowing them to microbially disintegrate into the soil thus eliminating the costs and concerns related to film retrieval and disposal. This renders the differential in the total application costs between PE and PHB copolymer mulch films to be considerably diminished compared to many other applications. Further, many countries and regions are beginning to introduce regulations banning the use of non-degradable films for mulching. In summary, this is an attractive market and application for Metabolix *Mirel*™ films, from functional, economic, environmental and regulatory perspectives.

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Comparison of different mulch materials in a tomato (*Solanum lycopersicum* L.) crop

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Abstract

Black polyethylene as mulch is the most extended material among vegetable growers; however, photodegradable and biodegradable films have appeared as an alternative to conventional mulches due to the risk of the progressive contamination of soils. Reflective materials reflect back most of the incoming solar radiation, being recommended in areas characterized by high soil temperatures. We compared the effect of three mulches, black polyethylene, black biodegradable corn starch plastic and aluminized photodegradable plastic on a tomato crop in an open field. We measured mulch deterioration, soil temperature under mulches, tomato yield and fruit quality attributes (total soluble solids, firmness, dry weight, juice content and shape). Biodegradable mulch performed its function successfully and disappeared visually from the soil about three months after the crop was finished. Photodegradable mulch deteriorated prematurely and polyethylene film was practically intact at the end of season. Significant differences in mean soil temperature under mulches were observed (27.8ºC in biodegradable, 28.7ºC in aluminized and 31.8ºC in polyethylene), although they did not have a marked effect on the crop yield. Marketable yields were similar in both biodegradable and polyethylene mulches (9.82 and 8.66 kg m^{-2}, respectively), and higher than those recorded in aluminized photodegradable mulch (6.85 kg m^{-2}), which resulted in the highest sunscald in fruits. No effect on the fruit quality attributes was observed. Biodegradable plastic mulches could be a good alternative to the traditional plastic films, and aluminized photodegradable mulches seem not very advisable because they reduce marketable yield and could increase the incidence of sunscald.

Additional keywords: biodegradable mulch, fruit quality attributes, photodegradable mulch, polyethylene mulch, reflective mulch, soil temperature, yield.

Resumen

Comparación de diferentes materiales de acolchado en un cultivo de tomate (*Solanum lycopersicum* L.)

El polietileno negro es el acolchado más utilizado por los horticultores; sin embargo, debido al riesgo de progresiva contaminación de los suelos, han aparecido materiales fotodegradables y biodegradables como alternativa a los convencionales. Los materiales reflectivos reflejan la mayor parte de la radiación solar incidente, siendo recomendados en zonas con altas temperaturas de suelo. Se ha comparado el efecto de tres acolchados, polietileno negro, plástico negro biodegradable de almidón de maíz y plástico aluminizado fotodegradable, en un cultivo de tomate al aire libre. Se ha controlado su deterioro visual, la temperatura del suelo, la cosecha y parámetros de calidad de los frutos (sólidos solubles, firmeza, peso seco, jugosidad y forma). El material biodegradable cumplió con éxito su función y desapareció visualmente unos tres meses después de finalizar el cultivo. El fotodegradable se deterioró rápidamente y el polietileno negro permaneció prácticamente intacto al final del ciclo. Se observaron diferencias significativa en las temperaturas medias del suelo bajo los acolchados (27,8ºC en biodegradable, 28,7ºC en aluminizado y 31,8ºC en polietileno), aunque sin marcado efecto sobre la cosecha. Las producciones comerciales fueron similares en biodegradable y polietileno (9,82 y 8,66 kg m^{-2}, respectivamente), superiores a las del aluminizado fotodegradable (6,85 kg m^{-2}), tratamiento con mayor incidencia de frutos asolanados. No se han observado diferencias en los parámetros de calidad del fruto. Los acolchados con plásticos biodegradables constituyen una buena alternativa a los tradicionales, mientras que los aluminizados fotodegradables no parecen aconsejables porque reducen la producción comercial y pueden incrementar el asolanado en frutos.

Palabras clave adicionales: acolchado biodegradable, acolchado fotodegradable, acolchado reflectante, parámetros de calidad, polietileno, producción, temperatura del suelo.

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Abbreviations used: BER (blossom-end-rot), CE (European Community), DAT (days after transplanting), LLDPE (linear low density polyethylene), LSD (least significant difference), sh (solar hour), SIA (Servicio de Investigación Agraria), TmoV (*Tomato mottle virus*).

Introduction

For decades, a common practice among the vegetable growers in Central Spain has been the use of non-degradable plastic mulches in open fields, mainly for spring-summer season vegetable crops such as tomato, pepper, melon, watermelon, etc., for a variety of reasons (Green *et al.*, 2003), summarized in an improvement in earliness, yield and fruit quality. Plastic mulches directly affect the microclimate around the plant by modifying the radiation budget of the surface and decreasing the soil water loss (Liakatas *et al.*, 1986), resulting in more uniform soil moisture and a reduction in the amount of irrigation water, which is very important for summer crops in this area. The soil temperature in the planting bed is raised, promoting faster crop development and earlier harvest (Lamont, 1993). Mulching decreases the fluctuations in temperature in the first 20-30 cm depth in soils and promotes root development, reduces vegetative competition in the rooting zone, reduces fertilizer leaching and soil compaction, and the vegetable productions are cleaner since no soil is splashed onto the plants or fruits (Ham *et al.*, 1993).

Polyethylene is one of the most commonly used plastic materials for mulching, due to the fact that it is easy to process, has excellent chemical resistance, high durability, flexibility and is odourless as compared to other polymers. It forms a relatively impermeable vapour barrier on the soil surface, changing the pattern of heat flow and evaporation (Tripathi and Katiyar, 1984).

The colour of the mulch largely determines its energy-radiation behaviour and its influence on the microenvironment surrounding the plants. The soil temperature under a plastic mulch depends on the thermal properties (reflectivity, absorptivity, or transmittancy) of a particular material in relation to the incoming solar radiation (Schales and Sheldrake, 1963; Tripathi and Katiyar, 1984), so colour affects the surface temperature of the mulch and the underlying soil temperature (Lamont, 1993). The degree of contact between the mulch and the soil also affects soil warming. The better contact the mulch has with the soil, the more effective the warming properties of the mulch (Lamont, 1996).

There are three primary non-degradable mulch types used commercially in the production of vegetable crops (Lamont, 1993): black, clear and the group of white, white-on-black and silver/aluminium reflective mulches. Black polyethylene is the most popular because it prevents weed growth and warms the soil in the spring, in addition to its low cost. Clear mulch provides an even warmer soil environment than black plastic mulch, but requires the use of another technique to control weeds (herbicide, soil fumigant or solarization). White, white-on-black and silver/aluminium reflective mulches can result in a slight increase or even a slight decrease in soil temperature compared to bare soil, tending to minimize changes in soil temperature, because they reflect back into the plant canopy most of the incoming solar radiation (Ham *et al.*, 1993; Csizinszky *et al.*, 1997). Therefore, these mulches are recommended when soil temperatures are high and any reduction in this parameter is beneficial for the crops (Lamont, 1993; Díaz *et al.*, 2001). Previous reports (Mahmoudpour and Stapleton, 1997) show that the increase of light reflectivity from the reflective mulch surface allows greater photosynthetic activity of the plants, and this effect is limited by crop development. Thus, when plant canopies develop to the point of completely covering the mulched beds, effective reflectivity of the mulches is reduced to near zero. Additionally, silver/aluminium reflective mulches are effective at repelling insect pests, especially aphids and thrips from vegetable crops (Riley and Pappu, 2000; Stapleton and Summers, 2002), which can serve as a vector for various viral deseases.

An important problem associated with the use of these non-degradable materials is the removal from the field at the end of the crop cycle. Plastic mulches do not break down and should never be disked or incorporated into the soil (Lamont, 1993), which implies a serious risk for the environment. However, the process of recovering and recycling them later is difficult as approximately 80% of the weight are non-plastic materials (González *et al.*, 2003). A large proportion of plastic films is left on the field or burnt by the farmers without legal control, emitting harmful substances with the associated negative consequences to the environment (Briassoulis, 2006; Scarascia-Mugnozza *et al.*, 2006).

In the early 1960's, photo- or biodegradable materials were recognized as one solution to the disposal problem associated with plastic mulches (Lamont, 1993). Photodegradable plastic breaks down under ultraviolet sunlight. The rate of breakdown depends on several factors such as temperature, the type of crops and the amount of sunlight received during the growing season. Thus, when photodegradable mulches are used under crops that cover less of the mulch (e.g., pepper) or in regions and seasons that receive high solar radiation, the mulch can be disintegrated prematurely and results useless. When using these materials it is necessary to lift the buried edges out of the soil and expose them to sunlight at the end of the season to favour their decomposition, and its effect on soil composition is not clear (Lamont, 1996; Greer and Dole, 2003).

For this reason, the use as mulch of biodegradable polymers formed from renewable resources is increasing in the last few years. These materials are basically composed of biopolymers, mainly polysaccharides such as cellulose and starch. Starch films, mostly from corn, potato and rice crops, are impermeable to water but permeable to water vapour and degrade into harmless products (CO_2 and water) when placed in contact with the soil humidity and microorganisms (fungi and especially bacteria) (Chandra and Rustgi, 1998). Therefore, these materials do not contaminate the environment and do not have to be removed from the land.

The aim of this study was to analyze the behaviour and deterioration of black polyethylene, aluminized photodegradable and black biodegradable mulches and to evaluate the effects on soil temperatures, yield and fruit quality of an open-field tomato crop.

Material and methods

Field site

The trial was conducted in 2003 at the experimental farm "Dehesa Galiana", belonging to the University of Castilla-La Mancha, in Ciudad Real (Central Spain) (4º2' W, 38º59' N, altitude 640 m). This area is characterized by a mediterranean continental climate. The total rainfall and mean temperature during the cropping seasons (June to October) were 167 mm (126 mm of which corresponding to October), and 22.5ºC, respectively, and the accumulated solar global radiation during the crop months was 3455.4 MJ m^{-2} (Table 1). The soil was loamy-clay (24.5% sand, 41.7% lime, 33.8% clay), with a normal level of organic matter (2.4%, Walkley-Black) and total nitrogen (0.133%, Kjeldahl), and very high contents of phosphorus (40.13 ppm, Olsen), assimilable potassium, calcium and magnesium (1.30, 36.0 and 4.0 meq 100 g^{-1}, respectively, ammonium acetate). The soil pH (1:2.5 water ratio) was 8.0 and the electrical conductivity (1:5 soil extract) 1.91 dS m^{-1}.

Experimental design and mulches

A randomised complete block design was adopted with three mulch treatments and three replications. The following mulch treatments were tested: black biodegradable film (Mater-Bi U-4, Novamont) 55 gauges (13.75 microns) thick, composed of a corn starch base, aluminized photodegradable (Deltalene) and black linear low density polyethylene (LLDPE) film (Siberline), both 60 gauges (15 microns) thick. Each basic plot consisted in one row 4 m length and 1.5 m apart, with plants separated by 0.5 m. The crop was daily irrigated by a trickle irrigation system, consisting in one low density polyethylene trickle line for each crop row (12 mm diameter) and emitters of 4 L h^{-1} separated by 0.50 m. After transplanting, about 30 mm of water were provided to favour crop establishment. Throughout the crop cycle, irrigation water amounts were applied following the methodology proposed by Allen *et al.* (1998), with a total of 520 mm.

Plant material and establishment

The study was performed using determinate fresh market tomato (*Solanum lycopersicum* L.) cv. Mina. Planting took place in the open field on 4 June, after placing by hand the mulches, using nursery seedlings with 3-4 mature leaves. The fragile consistency of the biodegradable film forced to prepare soil carefully. The crop cycle lasted 143 days after transplanting (4 June to 25 October).

Evaluation of mulch deterioration and soil temperature

The deterioration of the exposed mulching films was evaluated twice a month throughout the crop cycle by means of a visual rating scale, ranging from 1 to 9, where "1" indicated complete deterioration and "9" indicated no deterioration (film practically intact). At the end of the crop season, the biodegradable film was buried to favour its biodegradation by soil microorganisms.

From 25 June to 8 October, the soil temperature at a depth of 10 cm was determined in the middle of the beds under the different mulches and bare soil (no mulch) in each plot. Air temperature was measured at a height of 1.5 m above the soil. The measurements were realized at 6:30 solar hour (sh) in 16 dates with a needle soil digital thermometer (ThermoProbe). A further two sets of determinations were made on clear days during the vegetative growth and fruit set period (4 and 24 July), from 6:30 sh to 20:00 sh, at intervals of one and half hour. These soil values were compared to the air temperature at 1.50 m above the ground level.

Harvesting and yield component determinations

Red fruits were hand-harvested from 23 August (80 days after transplanting, DAT) to 25 October (143 DAT) in a total of ten harvests, controlling marketable, non-marketable and total yield, number of fruits and mean fruit weight.

At each harvest, marketable fruits (according to european commercial specifications, Regulation EC 790/2000) were size-graded into the standard sizes, considering the equatorial diameter of the fruit and assigning the following letters: MM (47-57 mm), M (57-67 mm), G (67-82 mm), GG (82-102 mm), GGG (>102 mm). Fruits in each size category were then counted and weighed.

Four marketable fruits were selected at random from each plot harvest to analyse different fruit quality parameters such as total soluble solids (ºBrix), firmness, dry weight, juice content and shape, defined as the ratio between the equatorial and the longitudinal diameter. The measurements of total soluble solids and fruit firmness were realized by a digital refractometer PR-32, Atago Co. LTD and a penetrometer Bertuzzi FT-327, Facchini, Italia, with a 8 mm plunger, respectively. Dry weight determinations were made in a forced air oven at 70ºC until constant weight.

In non-marketable yield, sunscalded and other non-marketable fruits (blossom-end rot, damaged, deformed and little fruits) were controlled. The incidence of sunscald in fruits was analysed separately due to the fact that this injury is caused by a combination of heat and light, being prevalent in high light environments (Wien, 1997), and probably the differences in reflecting the incident sunlight by the mulches employed could have any effect on it.

Statistical analysis

Statistical analysis (ANOVA, least significant difference, LSD test) was performed at a probability level $P<0.05$. Percentage data were arcsin transformed before analysis (Little and Hills, 1991).

Results

Behaviour of mulches

The first signs of mulch deterioration appeared on 10 June 2003 in the biodegradable film, only seven days after transplanting, when the global radiation accumulated by the mulch materials was of 236 MJ m^{-2}. However, in spite of these early cracks, this film behaved successfully, covering the soil until the crop shaded the mulch.

On 1 July (20 DAT) the aluminized photodegradable film presented important cross-sectional cracks, specially in the areas exposed to the solar radiation, while the deterioration was less in the areas of the mulch shaded by the crop. During these days, the average air temperature amplitude was of 18.0ºC, with maximum values of 21.0ºC. The solar radiation accumulated until this date was of 799 MJ m^{-2}.

Since then, the photo- and biodegradable mulches were gradually degrading, much more quickly the first one than the second. These cracks were used for weeds to grow, which were very numerous at the end of the crop cycle, especially in the aluminized photodegradable film, which presented the biggest cracks. During the harvest period, this material appeared divided in fragments, reaching an estimated soil cover of about 50%.

At the end of the season, the aluminized photodegradable mulch was highly deteriorated (deterioration in the visual rating scale of 1.0) and was not necessary to remove it from soil. In relation to the biodegradable film, despite the thickness and its peculiar consistency, it presented a positive behaviour and performed its function successfully (deterioration of 2.0). This material disappeared visually from the soil about three months after the crop finished, which could be favoured by the copious rainfall occurring during October (Table 1). Black polyethylene, however, remained practically intact (deterioration of 8.0). The solar global radiation accumulated throughout the crop cycle (4 June to 25 October) was 3363.6 MJ m^{-2}.

Soil temperature

The temperature of the air, bare soil and soil at a depth of 10 cm under each mulch during the crop cycle at 6:30 sh properly fits to a polynomial function of third degree (Fig. 1). The temperatures registered in bare soil

Table 1. Average air temperatures (mean, maximum, minimum), rainfall and global radiation during the growth cycle of the experiment

	Average air temperature (ºC)			Rainfall (mm)	Global radiation (MJ m^{-2})
	Mean	Maximum	Minimum		
June	25.5	34.3	16.8	0.6	852.1
July	25.6	35.5	15.7	0.0	897.8
August	25.9	35.0	16.7	14.7	751.3
September	21.2	29.4	13.1	26.0	605.9
October	14.1	18.9	9.3	126.0	348.3

were always lower than under mulch treatments, and the soil temperature under the different mulches was affected by the type of material employed. In the selected measuring dates during the crop cycle, soil temperatures were significantly higher (P<0.05) in black polyethylene at 35, 43, 50, 71, 83 and 119 DAT. The lowest values were obtained under the black biodegradable film, although without significant differences with respect to the aluminized photodegradable mulch.

Soil temperatures decreased sharply until 43 DAT in all of the treatments (Fig. 1). Since then, the values remained practically unchanged until 105 DAT, suffering a marked drop at the end of the crop season, in concordance with the air temperature.

The maximum values were obtained in the black polyethylene mulch up to 71 DAT. Since this date, the air temperature was higher than the soil temperature under mulches. The differences among treatments were smaller as the cycle went on, being practically inappreciable at the end of the experiment. The average soil temperatures reached at 6:30 sh throughout the crop cycle were 20.7ºC, 21.2ºC, 22.7ºC and 19.3ºC under black biodegradable, aluminized photodegradable, black polyethylene and bare soil, respectively.

In relation to the air and soil temperatures behaviour averaged across two daily periods (4 and 24 July), bare soil temperatures were always lower than under mulches, corresponding the highest values to black polyethylene (P<0.05) at all measurements times (Fig. 2). In relation to mulches, the lowest temperatures were always reached under the black biodegradable film, but no statistical differences with respect to the aluminized photodegradable mulch were noted in any case.

Maximum soil temperatures occurred near 15:30 sh in all the treatments (Fig. 2), ranging from 36.9ºC in black polyethylene to 31.0ºC in bare soil. Intermediate values were reached in black biodegradable (32.1ºC) and aluminized photodegradable films (33.7ºC). The lowest soil temperatures were registered at 6:30 sh.

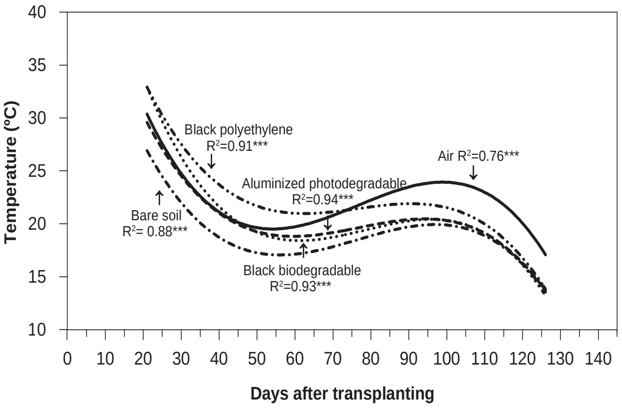

Figure 1. Evolution of temperature throughout the growth cycle in a tomato crop grown under different plastic films. Data measured at 6.30 solar hour. Soil temperature at a depth of 10 cm (temperatures averaged over three replications), air temperature at 1.50 m above ground.

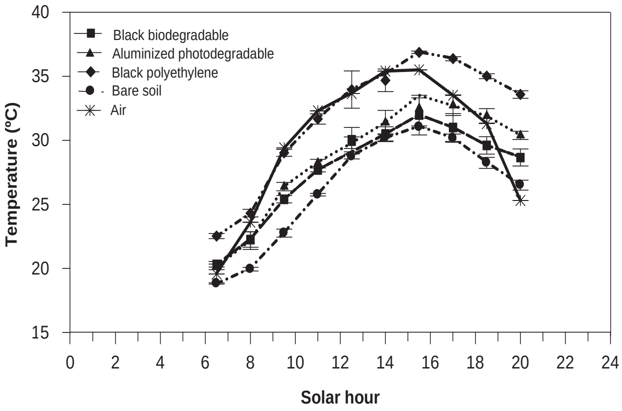

Figure 2. Diurnal patterns of air and soil temperatures averaged across two daily periods (4 and 24 July 2003). Soil temperature at a depth of 10 cm (temperatures averaged over three replications), air temperature at 1.50 m above ground. Vertical bars represent the standard error of the means.

Table 2. Average soil temperatures (mean, maximum and minimum), soil temperature amplitudes and excess mean soil temperature under mulches relative to bare soil (ΔT) averaged in two daily periods (4 and 24 July 2003) (ºC). Soil temperature at a depth of 10 cm (temperatures averaged over three replications)

	Average air temperature (ºC)			T amplitudes	ΔT
	Mean	**Maximum**	**Minimum**		
Black biodegradable	27.8 c	32.1	20.3	11.8 a	1.5 b
Aluminized photodegradable	28.7 b	33.7	20.1	13.6 a	2.5 b
Black polyethylene	31.8 a	36.9	22.5	14.4 a	5.6 a
Bare soil	26.2 d	31.0	18.8	12.2 a	-

Means followed by different letters in the same column are statistically different at $P<0.05$ (LSD test)

In all cases, the lowest values were obtained in black biodegradable and the highest ones in black polyethylene film (Table 2).

No statistical differences were found among the amplitudes (maximum less minimum data) of the diurnal soil temperatures measured (Table 2), being around 12.0ºC under black biodegradable and bare soil, but 13.6ºC and 14.4ºC under the aluminized photodegradable and black polyethylene films, respectively.

The daily mean soil temperatures registered under the biodegradable and the photodegradable films were only 1.5ºC and 2.5ºC higher than in bare soil, respectively, being up to 5.6ºC under the polyethylene mulch.

Yield and fruit quality

Marketable and total yields showed a similar behaviour related to the type of mulch employed, ranging from 6.85 to 9.82 kg m^{-2} and 7.43 to 10.33 kg m^{-2}, respectively (Table 2). Black biodegradable and polyethylene films were the most productive, without significant differences between them. Aluminized photodegradable film resulted in the lowest yields in both cases, with differences ($P<0.05$) with respect to the biodegradable mulch, being about 20% lower than that. The same trend was apparent in the number of fruits (Table 3), although no statistical differences were noted. In the same way, the type of mulch employed had no significant effect on marketable and total mean fruit weight (Table 3), although fruits of plants grown on the biodegradable film were slightly heavier than those of the other treatments, corresponding to the aluminized photodegradable film the lowest values in both cases. For this reason, the differences in yield among mulches were more marked than in number of fruits.

In relation to the non-marketable production (Tables 2, 3), the highest incidence of sunscald corresponded to the aluminized photodegradable film, with differences ($P<0.05$) with respect to the biodegradable mulch. In this last treatment, the injury was almost negligible. Aluminized photodegradable film multiplied by five the number of sunscalded in relation to the biodegradable mulch (Table 3), which represented an increase of the percentage of non-marketable fruits affected by this injury of 8.5 times. Intermediate values were attained in black polyethylene. Counts of blossom-end-rot (BER) fruits were practically inappreciable in all the treatments. For this reason, the BER fruits were added to the rest of the non-marketable fruit counts. The latter were

Table 3. Influence of mulch type on yield distribution according to the mulch treatments for a tomato crop grown in Central Spain

Mulch treatment	**Marketable**		**Non-marketable**						**Total**
			Sunscalded		**Others**		**Total**		
	kg m^{-2}	**%**	**kg m^{-2}**	**%**	**kg m^{-2}**	**%**	**kg m^{-2}**	**%**	**kg m^{-2}**
Black biodegradable	9.82 a	95.1 a	0.04 b	0.4 b	0.47 a	4.5 a	0.51 b	4.9 a	10.33 a
Aluminized photodegradable	6.85 b	92.2 a	0.25 a	3.4 a	0.33 a	4.4 a	0.58 b	7.8 a	7.43 b
Black polyethylene	8.66 ab	92.5 a	0.16 a	1.7 ab	0.54 a	5.8 a	0.70 a	7.5 a	9.36 ab
Mean	8.44	93.3	0.15	1.8	0.45	4.9	0.60	6.7	9.04

Means followed by different letters in the same column are statistically different at $P< 0.05$ (LSD test).

slightly higher in black polyethylene, although no significant differences were found with respect to the other treatments.

The evolution of the cumulative marketable fruit number and yield over the harvest period (Fig. 3) shows that the highest data were attained in black biodegradable and the lowest ones in aluminized photodegradable in both cases, being the differences more marked as the season advanced. Both biodegradable and polyethylene mulches presented similar values of the cumulative fruit number until 119 days after transplanting (Fig. 3a). Since this date, this parameter increased in a higher ratio in the biodegradable film. In relation to the cumulative marketable yield (Fig. 3b), the differences reached among mulches were bigger than in fruit number, showing the biodegradable film a more pronounced increase than the other treatments since 101 days after transplanting mainly as result of the increase in the mean fruit weight.

In relation to the partitioning of marketable yield into the different standard sizes (Table 4), in all the treatments the highest rate of fruits corresponded to the G size. The size distribution percentage was statistically similar in all the treatments except for GG, which was significantly higher ($P<0.05$) in the biodegradable mulch. Aluminized photodegradable and polyethylene films showed a certain trend to the smallest sizes (MM and M).

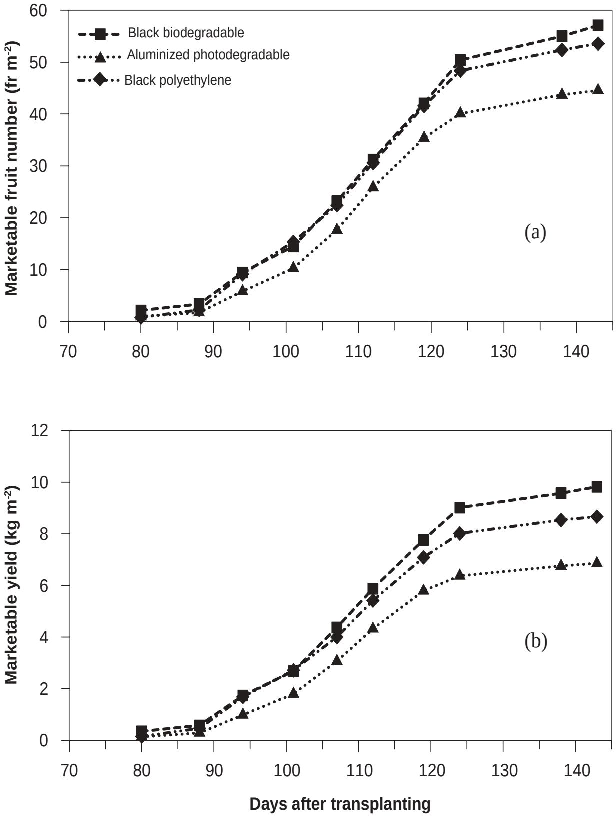

Figure 3. Evolution of the cumulative marketable fruit number (a) and yield (b) according to the mulch treatments for a tomato crop. Each point represents the average of three replications.

No significant differences among treatments were found in the quality attributes of marketable tomato fruits analyzed throughout the crop cycle (Table 5), resulting in similar values in shape, solid soluble solids, firmness, dry weight and juice content.

Discussion

Air temperature decreased more sharply at mid-afternoon compared to soil temperature due to the large heat capacity of the soil. The fluctuations of the air temperature throughout the day could cause a continuous dilatation/contraction process in the mulch materials. Consequently, the photodegradable mulch suffered important cross-sectional cracks early in the growing season and degraded prematurely; for this reason it was not necessary to remove it from soil at the end of crop cycle. Despite the thickness and the peculiar consistency of the biodegradable film, it performed its function successfully, disappearing visually from the soil a few months after the crop finished.

The effect of plastic coloured mulches on soil temperature has been widely studied (Streck *et al.*, 1995; Locher *et al.*, 2005; Lorenzo *et al.*, 2005; Moreno and Moreno, 2008). In general, plastic mulches increase soil temperature in relation to bare soil, these increases resulting higher in clear and dark materials than in the reflective colours such as white or silver/aluminium (Csizinszky *et al.*, 1997; Rangarajan and Ingall, 2001). In the latter, the temperatures can even be lower than in bare soil (Liakatas *et al.*, 1986; Lamont, 1996). The results obtained in this experiment support the previous studies; thus, the soil temperature in bare soil was always lower than under mulches, and the maximum soil temperatures were always reached under the black polyethylene film, followed by the aluminized mulch, because these last materials reflect back most of the incoming solar radiation (Ham *et al.*, 1993). For this reason, the reflective mulches are recommended to establish a crop when soil temperatures are high and any reduction in soil temperatures is beneficial (Lamont, 1996). The lowest soil temperatures were registered

Table 4. Influence of mulch type on fruit number distribution and mean fruit weight according to the mulch treatments for a tomato crop grown in Central Spain

Mulch treatment	**Fruit number**									**Mean fruit weight (g)**	
	Marketable		**Non-marketable**						**Total**		
			Sunscalded		**Others**		**Total**				
	Fr.m $^{-2}$	**%**	**Fr.m^{-2}**	**%**	**Fr.m $^{-2}$**	**%**	**Fr.m^{-2}**	**%**	**Fr.m^{-2}**	**Market.**	**Total**
Black biodegradable	57.07 a	88.9 a	0.36 b	0.6 b	6.76 a	10.5 a	7.12 a	11.1 a	64.19 a	173.6 a	162.1a
Aluminized photodegradable	44.44 a	85.7 a	1.81 a	3.5 a	5.61 a	10.8 a	7.42 a	14.3 a	51.86 a	156.8 a	146.7 a
Black polyethylene	53.56 a	86.8 a	0.89 b	1.4 b	7.22 a	11.7 a	8.11 a	13.2 a	61.67 a	163.9 a	151.8 a
Mean	51.69	87.2	1.02	1.8	6.53	11.0	7.55	12.9	59.24	164.8	153.6

Means followed by different letters in the same column are statistically different at $P < 0.05$ (LSD test).

under the biodegradable film in all the cases, which could be explained by the composition of this material, which permits increasing gas exchange with the open air as result of its higher permeability to water vapour (Chandra and Rustgi, 1998). Moreno and Moreno (2008) obtained similar results by comparing some biodegradable and polyethylene mulches of different colours, indicating that the differences in soil temperature among mulches were firstly due to the composition of the film.

The greatest soil temperature differences among treatments occurred early in the growing season (Fig. 1), before plant growth became sufficient to shade the row surface, in agreement with previous researchers (Schales and Sheldrake, 1963; Streck *et al.*, 1995; Brault *et al.*, 2002). Thus, the lowest incident solar radiation due to the progressive covering of the mulch by the crop and the gradual deterioration of the mulch materials throughout the crop cycle could have reduced the influence of the type of mulch on soil temperature. These aspects, linked to the end of the summer season, caused that these values tended to be similar to those obtained in bare soil at the end of the growing season.

Marketable and total yields were similar in both black biodegradable and polyethylene mulches, in agreement with Martín-Closas *et al.* (2003) in a tomato crop. The increased yield was the result of a slight increase in the number of fruits, which were also slightly heavier and larger, especially in the biodegradable treatment, than those obtained in the photodegradable mulch.

The range of temperatures registered under the different mulches in this experiment did not have a marked effect on the crop yield. Tindall *et al.* (1991) and Grass-

Table 5. Distribution of marketable yield into the standard sizes according to the mulch treatments for a tomato crop grown in Central Spain. MM: 47-57 mm, M: 57-67 mm, G: 67-82 mm, GG: 82-102 mm, GGG: >102 mm

Mulch treatment	**MM**		**M**		**G**		**GG**		**GGG**	
	kg m^{-2}	**%**	**kg m^{-2}**	**%**	**kg m^{-2}**	**%**	**kg m^{-2}**	**%**	**kg m^{-2}**	**%**
Black biodegradable	0.33 a	3.34 a	1.84 a	18.78 a	5.18 a	52.81 a	2.40 a	24.47 a	0.06 a	0.60 a
Aluminized photodegradable	0.63 a	9.13 a	1.56 a	22.83 a	3.37 a	49.22 a	1.29 b	18.83 a	0.00 a	0.00 a
Black polyethylene	0.37 a	4.31 a	2.04 a	23.58 a	4.72 a	54.49 a	1.48 b	17.06 a	0.05 a	0.57 a
Mean	0.44	5.59	1.81	21.73	4.42	52.17	1.72	20.12	0.04	0.39

Means followed by different letters in the same column are statistically different at $P < 0.05$ (LSD test).

Table 6. Average quality parameters of marketable yield according to the mulch treatments for a tomato crop in Central Spain

Mulch treatment	Shape (D/L)	Total soluble solids (ºBrix)	Firmness (kg cm^{-2})	Dry weight (%)	Juice content (%)
Black biodegradable	0.83 a	4.14 a	5.15 a	4.14 a	64.3 a
Aluminized photodegradable	0.84 a	3.92 a	5.17 a	4.01 a	66.9 a
Black polyethylene	0.84 a	4.01 a	5.09 a	3.84 a	66.4 a
Mean	0.84	4.02	5.14	4.00	65.87

D/L: ratio between the equatorial (D) and the longitudinal (L) fruit diameter. Means followed by different letters in the same column are statistically different at $P < 0.05$ (LSD test).

baugh *et al.* (2004), testing organic and inorganic mulches in a tomato crop, observed that although plastic mulches produced the maximum soil temperatures, they were probably harmful to the plants, resulting in the lowest marketable and total yield compared to the organic treatment. Similar results were obtained by Streck *et al.* (1995) with different plastic mulch materials in a tomato crop. However, Decoteau *et al.* (1989) and Abdul-Baki *et al.* (1992) attributed the highest tomato yields, in part, to the highest temperatures reached under the mulches tested.

The lowest marketable and total yield obtained in the reflective photodegradable mulch could be attributed to its early breakage, showing important cracks, which allowed the weeds to grow, competing with the crop for light, water and nutrients. Another aspect derived from the early degradation of this material could be the increase in water losses by evaporation from the soil surface. Suwwan *et al.* (1988) and Streck *et al.* (1995), when comparing opaque and reflective mulches, observed that tomato yield was not significantly affected by the type of mulch employed. Csizinszky *et al.* (1997) and Mahmoudpour and Stapleton (1997), however, obtained significantly higher yields in reflective mulches than in all the other treatments, probably due to the fact that the materials tested in those experiments were not photodegradable and covered completely the soil until the end of the crop cycle. Csizinszky *et al.* (1997) also associated the highest yield in silver mulch to lower soil temperature and greater photosynthetically active radiation reflected from the mulch onto the plants, also reducing the high populations of whitefly-transmitted *Tomato mottle virus* (TMoV).

The small and sharp cracks presented in the biodegradable film only allowed a little spread of weeds, so this factor did not exert the same influence on this material.

In relation to the non-marketable production, the aluminized photodegradable film resulted in the highest incidence of sunscald, in agreement with Suwwan *et al.* (1988). It could be explained by the property of these materials to reflect an important ratio of the incident solar radiation, as previously noted, which could increase fruit pericarp temperatures exceeding 40ºC, temperatures which are considered as critical by Kinet and Peet (1997) for sunscald in tomato fruits. In despite of the early deterioration of this material, remained fragmented on the soil during the harvest period and its reflective effect could favour sunscald in fruits.

The calculated percentages of marketable and non-marketable yield and fruit number relative to the total values were similar in all treatments. Thus, the treatments more productive (black biodegradable and polyethylene) increased the marketable and non-marketable yield and number of fruits in a similar manner as compared with the less productive (aluminized photodegradable), in concordance with Suwwan *et al.* (1988).

The type of mulch employed had no effect on the fruit quality parameters measured, in concordance with Martín-Closas *et al.* (2003), who neither found significant differences in shape nor soluble solid content in processing tomato fruits by comparing black polyethylene to biodegradable mulches.

The results obtained suggest that the use of biodegradable films as mulching could be a good alternative to the traditional plastic films widely used in Central Spain, especially in spring-summer crops, as long as the early deterioration does not prevent them performing correctly all their functions. These materials do not cause a reduction of the productive capacity of the plants and degrade rapidly, avoiding all the problematic aspects derived from the use of polyethylene as mulch. For the other hand, the use of aluminized photodegradable mulches in these conditions seems not very advisable because they reduce marketable yield and the size of fruits, and could increase the incidence of sunscald.

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Penn State Extension

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Biodegradable Mulches

Tianna Dupont, Penn State Cooperative Extension

“I value my time too much to want to spend it ripping up plastic in the fall,” is Andrew Frankenfield’s reason for trying biodegradable mulches. Andrew is a Penn State Extension educator in Montgomery County, and he is also a farmer. He tried a half acre of biodegradable mulch this year for tomatoes. “So far it looks good, it is starting to degrade along the sides but the weeds are not breaking through,” he told a group of 50 farmers at a field day at Trauger Farms in Kintnersville, PA this month. As we looked at the four biodegradable mulches planted to tomatoes I heard a great discussion of the benefits and disadvantages.

We all know the benefits of plastic mulch. Not only does it keep the weeds down, it warms up the soil giving us earlier (and more) tomatoes, peppers, eggplants and other heat loving veggies. But it costs us. Farmers estimate it costs $25-100 an acre for labor and disposal of plastic mulch.

A possible alternative to black plastic mulch is biodegradable film mulches that look and act much like black plastic, but instead of ripping them up in the fall, you till them into the soil and the microbes degrade the material, leaving you a clean field (hopefully) in the spring.

Good biodegradable mulches are made from starch (corn or wheat). The starch is food for the microbes. They eat it and turn it into CO_2 and water. The material will break down fastest when the microbes are most active – when the soil is warm and moist. An important thing about starch based mulches is they become sticky and adhere to the soil as they break down, instead of becoming brittle and blowing around like some of the older technology.

Some of you may have experienced biodegradable mulches in the past and say no way –too hard to lay with the plastic layer – stuck around for ages – too expensive. . . . .Well it may be time to look again. Some of the new mulches are performing well in research trials. One product (Biotelo) had good soil stretch and field application similar to plastic. The soil temperature and yields for muskmelon were similar to plastic according to a study by Dr. Rangarajan at Cornell. In a more recent trial from Dr. Orzolek at Penn State in pepper, cantaloupe, eggplant, zucchini all had as good or better yields with biodegradable mulch films (various brands). Even though the film began to degrade before the crop matured, there was no weed growth or competition.

But the question remains – are the biodegradables economical? I sat down with my neighbor to run a few numbers. He figures he uses about 7,000 feet of plastic per acre (1,000 ft rows, 6 ft centers). For the cheapest of the biodegradable mulches I found that is a little less than one 8,000 ft roll at **$349/ A for biodegradable mulch**. Regular plastic mulch runs him $95 per 4,000 ft roll. At two rolls per acre it costs him **$200/ A for plastic mulch.** But that does not take into account the cost of ripping up the plastic and disposal. He just pulled up an acre this morning. In two hours for three guys, plus the tractor operator, it cost him about $100 per acre. Disposal in this area is about $50/ Ton. For about 400 lbs/ A of plastic disposal is another $10/ A. Including these extra costs that is **$310/ A for plastic mulch plus removal and disposal**. That does not include the time and hassle to dispose of it.

I don't think the final word is in on biodegradable mulches. But it looks like they are worth experimenting with.

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Biodegradable Mulches

Why think about Biodegradable Mulches?

- Growers estimate labor + disposal of plastic =$25-$100/ A.
- Biodegradable mulches can be tilled in at the end of the season reducing labor and disposal costs.

What are Biodegradable Mulches?

- Good biodegradables are made from plant starches such as corn and wheat.
- Soil microbes break down the starch into CO2 and water.
- Warm, moist conditions that favor the microbes speed up biodegradation.
- Sticky starches help them adhere to soil, keeping them from blowing away/ littering.
- Other degradable films are made from polyethylene which degrades slowly.

WeedGuard Plus – Non Fert - Sunshine Paper Co

- OMRI listed
- Weed Guard Plus – Fert contains 5-5-5

<u>Notes from Orzolek 2008</u>

- Paper tore when press wheels were angled.
- Paper dried and stayed intact after rain.
- Soil temp 2” deep (Jul14) was 84 F vs. 79 F under black non-degradable plastic.
- Yield compared to non-degradable plastic
  - Cantaloupe was the same (32/ 27 lbs vs. 42 lbs/ 100 ft).
  - Acorn squash was 36% higher with paper + 5-5-5.
  - Pepper yield was lower (18-21 vs. 38 fruit/ 100 ft).
  - Eggplant yield was lower (14/21 vs. 34 fruit/ 100 ft).

<u>Notes from Cave Moose Farm SARE Project</u>

- Cost per ft including materials and labor for laying, maintaining, removing and disposing
  - $0.34 – 0.35/ ft paper
  - $0.19-0.20/ ft Agrofilm
  - $0.20-$.21/ ft plastic

Mater-bi Agromulch (Biotelo) – Novamont Agrofilm – biobag

- Corn starch base
- Compostable
- Approved for use by IFOAM (European Organic)

<u>Notes Rangarajan 2006</u>

- Field application similar to plastic
- Good soil stretch
- Soil temperature similar to plastic
- Similar yields to plastic for muskmelon
  - Total T/A – 14 (plastic), 13 (Biobag), 12.2 (Materbi), 15 (Materbi brown)
  - Early Season T/A – 3.5 (plastic) vs 1.6-2.8 (biodegradables)

<u>Notes from Cave Moose Farm SARE Project</u>

- “The material began to degrade by mid-summer. . .(but) the ground underneath remained bare.”
- Yield per dollar spent was better w/ plastic for winter squash but higher w/ Agrofilm for pumpkins.

<u>Notes from Orzolek 2007, 2008</u>

- Biodegradable performed as good or better than plastic for yields in pepper, cantaloupe, eggplant, zucchini (ie 30-40 lb peppers/ 24 ft).
- No weed growth/ competition when film degraded before crop matured.

Metabolix

- Resins from plant derived sugars
- Experimental films #7, #13, #19 (black), #23 (clear)

Notes from Orzolek 2009

- New mulches are more flexible and did not tear.
- Did not start to degrade until 14 days after application.
- Brittle pieces tended to blow off site.
- Pepper, cantaloupe and acorn squash produced lower yields on biodegradable (Metabolix).
- Even after biodegradable plastic began to break down, no weeds were seen on the bed.
- Incorporation of the remaining mulch by roto-tilling increased degradation.

Local 2010 Commercial Sources and Prices

Nolts Produce Supply
152 North Hershey Avenue
Leola, PA 17540-9711
(717) 656-9764

Biotelo	4’ x 5,000’ roll	.6 ml	$385
Biotelo	5’x 4,000’ roll	.6 ml	$369
Eco 1	4’ x 8,000’ roll	.6 ml	$349
Plastic	4’x 5,000’ roll	1ml	$95.5

Rainflo
884 Center Church Road
East Earl, PA
(717) 445-6976

Biotelo	4’ x 5,000’ roll	.6 ml	$369
Biotelo	5’x 4,000’ roll	.6 ml	$369
Weed Guard Plus	48” x 1000’ roll		$141
Weed Guard Plus (fertilized)	48” x 1000’ roll		$327
Plastic	4’x 4,000’ roll	1ml	$90

Prepared by Tianna DuPont, Sustainable Agriculture Educator, Northampton and Lehigh Counties.