PETITION FOR LISTING
ON
NATIONAL LIST OF APPROVED AND PROHIBITED
SUBSTANCES
SEC. 2118. [7 U.S.C. 6517] NATIONAL LIST

Petitioner name: Aquaculture Working Group, % George S. Lockwood, Chair
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Date of petition: April 27, 2012

Check applicable:

) § 205.609 Synthetic substances allowed for use in organic aquatic *plant* production.

) § 205.610 Nonsynthetic substances prohibited for use in organic aquatic *plant* production

X § 205.611 Synthetic substances allowed for use in organic aquatic *animal* production.

) § 205.612 Nonsynthetic substances prohibited for use in organic aquatic *animal* production.

Send to: National List Coordinator, National Organic Program,
USDA/AMS/TM/ NOP, Room 4008–So., Ag Stop 0268,
1400 Independence Ave., SW.,
Washington, DC 20250.

Summary of request:

Previous actions by NOSB and NOP allow tocopherols in the organic production of livestock under:

§ 205.603 Synthetic substances allowed for use in organic livestock production.
(d) As feed additives.
(3) Vitamins, used for enrichment or fortification when FDA approved.

and

§ 205.605 Nonagricultural (nonorganic) substances allowed as ingredients in or on processed products labeled as “organic” or “made with organic (specified ingredients or food group(s)).
(b) Synthetics allowed:
Tocopherols—derived from vegetable oil when rosemary extracts are not a suitable alternative.

This petition is a request for NOSB and NOP to allow tocopherols in the organic production of aquatic animals in:

> "§ 205.611 Synthetic substances allowed in organic aquatic animal production
>
> (*x*) Tocopherols."

For many years, synthetic tocopherols have been allowed in terrestrial organic livestock production in § 205.603 as a vitamin feed additive, and in § 205.605(b) as a processed food antioxidant.

This is a petition to allow tocopherols as an antioxidant in feed for aquatic animals. Most aquatic animals require fish oil, or certain omega-3 fatty acids, for healthy growth, but these lipids rapidly oxidize if not protected. Likewise, most aquatic animals require fish meal and other feed ingredients that must be protected against oxidation.

In conventional aquaculture, the preferred anti-oxidant is ethoxyquin, a synthetic substance. Other synthetic alternatives to tocopherols include butylated hydroxyanisole (BHA), butylhydroxytoluene (BHT), and tertiary butyl hydroquinone (TBHQ). However, for organic production tocopherols are favored.

It is understood that mixed tocopherols are in regular use as antioxidants in fish meal as a feed ingredient in organic poultry production.

In addition to using antioxidants for protecting the nutritional value of fish oil and fish meal as a feed ingredient for aquatic animals, it is important to note that the International Maritime Dangerous Goods Code of the International Maritime Organization classifies fish meal as hazardous cargo. The U.S. Coast Guard requires antioxidants such as mixed tocopherols to be added to fishmeal for safety reasons to prevent combustion. Upon entry to a U.S. port, the Coast Guard requires proof of antioxidant.

Nearly all fishmeal producers tributary to the United States , including those producing fishmeal domestically, apply antioxidant to fishmeal during processing for quality control purposes.

Such regulations are due to the generation of considerable heat in untreated fishmeal to the point of fire due to aerial oxidation of the active chemical sites on fish oil molecules. The oxidation reactions are associate with the product of heat. This problem is dealt with by rendering fish meal to be less susceptible to oxidation by treating with antioxidants. The milled meal is cooled and treated with antioxidants such as ethoxyquin, usually by spraying the meal as it passes through a trough. Mixed tocopherols are also employed for this purpose. More information can be obtained at:

http://www.ukpandi.com/fileadmin/uploads/uk-pi/LP%20Documents/Carefully_to_Carry/Fishmeal%20cargoes%20self%20heating.pdf

and

http://www.airseacontainers.com/index.php/hazmat-publications/imo-imdg-code.html .

1. The substance's chemical or material common names.

Tocopherols are a class of chemical compounds of which many have vitamin E activity. *Gamma*-tocopherol is the most common form in the American diet due to a higher intake of soybean and corn oil. Tocopherols are fat-soluble antioxidants but also seem to have many other functions. Tocopherols occur in alpha, beta, gamma and delta forms, determined by the number and position of methyl groups on the chromanol ring. Most natural vitamin E supplements are derived from vegetable oils, usually soybean oil. Tocopherols are used as a preservative to delay the onset of rancidity in fats and oils, and thereby to extend shelf life.

2. The manufacturer's or producer's name, address and telephone number and other contact information of the manufacturer/producer of the substance listed in the petition.

There are many suppliers of tocopherols, including but not limited to Archer Daniels Midland Company, Kemin Industries Inc., Alltech, and Wilmar.. There are no tocopherols specifically manufactured for use in aquaculture.

3. The intended or current use of the substance such as use as a pesticide, animal feed additive, processing aid, nonagricultural ingredient, sanitizer or disinfectant. If the substance is an agricultural ingredient, the petition must provide a list of the types of product(s) (*e.g.*, cereals, salad dressings) for which the substance will be used and a description of the substance's function in the product(s) (*e.g.*, ingredient, flavoring agent, emulsifier, processing aid).

Tocopherols a feed additive for aquatic animals as an anti-oxidant. They are mixed with fish oil, fish meal, nutritional pigments, and various grains and lipids that are included as feed ingredients. For example, mixed tocopherols are added to fish meal in the amount of 300 to 600 ppm (0.03% to 0.06%). In cases of very high fat content higher levels may be required. In the case of fish oil, levels of 0.2% and above are used.

Many factors affect lipid oxidation such as the composition of fatty acids (presence of polyunsaturated fats), other ingredients present, moisture content, packaging etc. Therefore, it is comment practice to conduct shelf stability tests to determine the appropriate level for each application.

4. A list of the crop, livestock or handling activities for which the substance will be used. If used for crops or livestock, the substance's rate and method of application must be described. If used for handling (including processing), the substance's mode of action must be described.

Most feeds for aquatic animals require some amounts of fish oil, or fish oil substitutes of other lipids due to the extremely digestible nature of fish-derived products and the short length of many animals' digestive tracts, particularly in early stages of life. Fish oil and many fish oil substitutes must be protected against oxidation.

Oxidized or rancid lipids in fish feeds cause a decrease in nutritive value and can be detrimental to animals' metabolic regulation. In order for the good health and growth of many fish species, it is necessary to protect the lipids against oxidation. Rancid lipids fed to fish are also unhealthy for human consumers. Therefore, anti-

oxidants are necessary in fish feeds. In the absence of anti-oxidation activity, the oxidation of lipids in fish meal can generate sufficient heat to cause the fish meal to ignite.

Antioxidants are chemical compounds that are added to feed ingredients to control and delay the oxidation of lipids. Other food components, such as carotenoid pigments can also undergo oxidation. The mechanism of highest concern in feed manufacturing is autoxidation, also known as atmospheric oxidation, which is the oxidation of unsaturated fatty acids, resulting in products that produce off flavors and off odors. In fish products, the most nutritive fatty acids that need preservation are highly unsaturated. The rate of autoxidation of lipids can be accelerated by an increased radiation level, divalent cation concentration, temperature, and oxygen concentration.

Autoxidation of lipids is a process involving three steps. The first step involves the formation of free radicals and is called initiation. Initiation is enhanced by a number of factors, including light, heat, UV radiation, and the presence of divalent cations, such as copper and iron, known as pro-oxidants. The second step in autoxidation is called propagation and involves the reaction of free radicals formed in the initiation step with more free double bonds on fatty acids, forming a number of secondary product sand radicals. The final step is termination, in which free radical production slows, and finally stops; various secondary products of fatty acid oxidation react in various ways to form stable end products.

Because the propagation step itself forms more free radicals than it uses, autoxidation reactions are autocatalytic, meaning that once oxidation starts, it continues at an accelerating rate until substrates (double bonds) are used up. The number of free radicals formed from oxidation of individual fatty acids is related to the number of its double bonds, making oxidation of the fatty acids in fish oils (very unsaturated) a much more rapid process than oxidation of less unsaturated lipids.

Antioxidants work by chelating pro-oxidant divalent cations, by acting as free radical acceptors, or by donating hydrogen. The latter two functions are considered sacrificial because once an antioxidant molecule reacts, it no longer possesses antioxidant properties and is therefore "destroyed" in the process. Thus, antioxidant concentrations fall during the initiation phase, and once they are used up, oxidation reactions proceed very rapidly.

Antioxidants added to lipids and feeds to prevent oxidation by reacting with free radicals are phenolics, such as butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA), and amines, such as ethoxyquin. BHA and BHT are added to feeds at a level of 0.1%, while ethoxyquin is added at 0.015%. Other antioxidants in use include dilaury l thiodi propionate, propyl gallate, and thiodipropionate. Antioxidants that prevent oxidation by chelating metallic pro-oxidants include ascorbic acid, phytic acid, tartaric acid, oxalic acid, and ethylenediaminetetraacetic acid (EDTA). There is a synergistic effect when phenolicor amine antioxidants are combined with an antioxidant that chelates pro-oxidants.

Many plant sources of lipids contain naturally occurring antioxidants, mainly tocopherols. These compounds inhibit autoxidation of lipids until they are used up,

at which time the rate of oxidation reactions increases very rapidly. The period of time during which antioxidants prevent oxidation is called the induction time. Chemical tests to detect lipid oxidation, such as peroxide values and TBARS, cannot measure induction time, and low values from these tests can give a false sense of security to a feed company. By testing a lipid source or feed before and after an accelerated oxidation test, such as the Schaal Oven Storage Stability Test [http://www.eastman.com/Literature_Center/Z/ZG194.pdf] , the induction time can be estimated, and appropriate precautions taken to avoid oxidation. In addition to the Schall Test, other tests are in common use.

The above is taken from http://aquafind.com/articles/Feed-Additives.php 7. Antioxidants.

The Schaal Oven Stability Test is described in:

Wan, P.J., Accelerated Stability Methods, in *Methods to Assess Quality and Stability of Oils and Fat-Containing Foods*, edited by K. Warner and N.A.M. Eskin, AOCS Press, Champaign, Illinois 1995, pp.179–189.

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. Petitioners with concerns for confidential business information may follow the guidelines in the Instructions for Submitting CBI listed in #13.

Mixed tocopherols are extracted from soybean oil with solvent extraction, and soybean oil is extracted from beans with solvent extraction. Hexane is commonly used as a solvent, although others solvents can include ethanol, isopropanol, acetone, isopentane, isohexane and trichloroethylene.

Further information on the extraction and refining of tocopherols from vegetable oils can be obtained at:
http://cdn.intechopen.com/pdfs/15722/InTech-Effect_of_refining_process_and_use_of_natural_antioxidants_on_soybean_oil.pdf

6. A summary of any available previous reviews by State or private certification programs or other organizations of the petitioned substance. If this information is not available, the petitioner should state so in the petition.

Organic Materials Review Institute (OMRI)

Tocopherols
Status: Allowed
Class: Processing Non-agricultural Ingredients and Processing Aids
Origin: Synthetic Nonagricultural
Description:
Must be derived from vegetable oils when rosemary extracts are not a suitable alternative. See also VITAMINS – NUTRIENT for use of tocopherols as a vitamin.
NOP Rule: 205.605(b)

Tocopherols
Status: Allowed with Restrictions

Class: Livestock Feed Ingredients, Livestock Health Care
Origin: Synthetic/Nonsynthetic
Description:
Source of vitamin E. Includes mixed tocopherols and alpha-tocopherol (alpha-tocopheryl) acetate. See also VITAMINS.
NOP Rule: 205.237(a), 205.237(b)(2) & 205.603(d)(3)

Vitamin E
Status: Allowed with Restrictions
Class: Livestock Feed Ingredients, Livestock Health Care
Origin: Synthetic/Nonsynthetic
Description:
May be derived from mixed tocopherols and alpha-tocopherol (alpha-tocopheryl) acetate. See also VITAMINS and Appendix A: Livestock Vitamins and Minerals.
NOP Rule: 205.237(a), 205.237(b)(2) & 205.603(d)(3)

Fish Oil
Status: Allowed with Restrictions
Class: Processing Agricultural Ingredients and Processing Aids
Origin: Nonsynthetic Agricultural
Description:
Stabilized with organic ingredients or only with ingredients on the National List, §§205.605 and 205.606. Nonorganic sources may be used in or on processed products labeled as "organic" only when not commercially available in organic form. See AGRICULTURAL INGREDIENTS – NONORGANIC for more information on the use of nonorganic agricultural ingredients.
NOP Rule: 205.301(b),(c),(f) & 205.606(f)

Fish Meal
Status: Allowed with Restrictions
Class: Livestock Feed Ingredients
Origin: Nonsynthetic
Description:
Fishmeal may be used as a feed additive or feed supplement at or below the amount needed for adequate nutrition for the species at its specific stage of life. Fishmeal may be preserved with natural substances and substances that appear on the National List for use in livestock feed production, provided such substances are not restricted to prevent this use and are permitted by FDA regulations.
NOP Rule: 205.237(a), 205.237(b)(2) & 205.238(a)(2)

Fish Meal
Status: Prohibited
Class: Livestock Feed Ingredients
Origin: Nonsynthetic
Description:
Fishmeal that is preserved with synthetic substances that do not appear on the National List for use in livestock feed production or with natural substances not permitted by FDA regulations are prohibited for use as a feed additive or feed supplement.
NOP Rule: 205.105(a) & 205.237(b)(6)

7. Information regarding EPA, FDA, and State regulatory authority registrations, including registration numbers. If this information does not exist, the petitioner should state so in the petition.

FDA – Generally Regarded As Safe.

Canadian Organic Aquaculture Standrads (Draft) Organic Aquaculture Working Group Fisheries and Oceans Canada
Antioxidants Non-synthetic sources only. Water, alcohol, acid and base extracts permitted by this standard, CAN/CGSB 32.310 and CAN/CGSB 32.311only. Synthetic sources are permitted when legally required.

Naturland (Germany)
8.7. Upon approval by Naturland, natural antioxidants (e. g. tocopherol) may be added to the feed.

Soil Association (UK)
30.8.4 You may use antioxidants of natural origin.

8. The Chemical Abstract Service (CAS) number or other product numbers of the substance and labels of products that contains the petitioned substance. If the substance does not have an assigned product number, the petitioner should state so in the petition.

There are many mixed tocopherol products available. Many are mixed with other substances. Cited below are essentially pure mixed tocopherol products produced by Archer Daniels Midland Company and Kemin.

		Weight %	CAS-No
ADM Decanox MTS – 90	Mixed Tocopherols	100	1406-66-2
ADM Decanox MTS – 90G	Mixed Tocopherols	100	1406-66-2
Kemin Naturox IPO	Mixed Tocopherols	100	(not established)

Individual tocopherols are coded as CAS:

59-02-9 (alpha tocopherol);
16698-35-4 (beta-tocopherol;
119-13-1 (delta-tocopherol); and
54-28-4 (gamma-tocopherol)

9. The substance's physical properties and chemical mode of action including (a) Chemical interactions with other substances, especially substances used in organic production; (b) toxicity and environmental persistence; (c) environmental impacts from its use and/ or manufacture; (d) effects on human health; and, (e) effects on soil organisms, crops, or livestock.

Scientific and other literature is replete with information that omega-3 fatty acids contained in fish and fish oil beneficially impacts human health in many respects, including the prevention of cardiovascular disease, mental health, cancer, etc. Unfortunately, these highly unsaturated fatty acids, when they come in contact with air, readily oxidize into harmful substances. Therefore, it is common practice in aquaculture to treat fish oil and fish meal with antioxidants.

An antioxidant may be defined as a substance which, in relatively low concentration, markedly inhibits the rate of the reaction with oxygen (Stansby 1967, Mar-

kley 1961). Information about this phenomenon is particularly important with fish oil, the fatty acids of which are generally highly unsaturated and hence unusually susceptible to attack by the oxygen of air (Stansby 1967). Antioxidants are those substances that interfere either with the initiation step or with the early stages of the propagation steps. An antioxidant reacts with either the original free radical or with one formed in the early stages to give an intermediate, which is not capable of continuing the chain.

Oxidation of lipids not only produces rancid odors and flavors, but also can decrease nutritional quality and safety by the formation of secondary products (Frankel 1996). The products of lipid oxidation are known to be health hazards since they are associated with aging, membrane damage, heart disease and cancer (Suja *et al*. 2004). The consumption of such oxidized fats has been reported to cause diarrhea, liver enlargement, growth depression and histological changes in tissues of experimental animals (Nwanguma *et al*. 1999). The production of biologically active carbonyl compounds including acrolein, malonaldehyde (MA) and 4-hydroxyl-2-nonenal (4-HN) from lipids during oxidation has been reported by many researchers (Miyake and Shibamoto 1996). These chemicals have been associated with human diseases such as atherosclerosis, cataracts and ageing.

Fish oils are highly sensitive to oxidative deterioration, which entails practical problems. During the autoxidation of fish oils, undesirable flavors and odors develop at very low peroxide values, even during the induction period. Oxidation of lipids not only produces rancid odors and flavors, but can also decrease nutritional quality and safety by the formation of secondary products. In order to solve the problem, research for safer and effective natural antioxidants are underway and several natural sources are being examined.

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. If this information does not exist, the petitioner should state so in the petition.

See Appendix A and B.

11. Research information about the substance which includes comprehensive substance research reviews and research bibliographies, including reviews and bibliographies which present contrasting positions to those presented by the petitioner in supporting the substance's inclusion on or removal from the National List. For petitions to include non-organic agricultural substances onto the National List, this information item should include research concerning why the substance should be permitted in the production or handling of an organic product, including the availability of organic alternatives. Commercial availability does not depend upon geographic location or local market conditions. If research information does not exist for the petitioned substance, the petitioner should state so in the petition.

Chol Su Pak and Margrét Bragadóttir, Stability and Quality of Fish Oil During Typical Domestic Application (2005) at: http://www.unuftp.is/static/fellows/document/pak05prf.pdf

Covi-ox product description sheet at:
http://www.cognis.com/NR/rdonlyres/FEFD1124-ECF6-41D1-B8F9-5628EDA13241/0/FISHOIL.PDF

J.K. Kaitaranta, Control of lipid oxidation in fish oil with various antioxidative compounds, Journal of the American Oil Chemists' Society, 1992, Springer at: http://www.springerlink.com/content/p37r5rm5017p10w0/ .

Mark Sewald and Jon DeVries, Food Product Shelf Life, Medallion Labs paper attached as Appendix C.

TAP Reviewer Comment Form, 8-28-95 by Dr. Richard C. Theuer, at:
http://www.ams.usda.gov/AMSv1.0/getfile?dDocName=STELPRDC5088849

NATURAL & SYNTHETIC Alpha-tocopheryl acetate is the principal commercial form of Vitamin E for food fortification, dietary supplementation and medicinals, and for domestic animals.

Concentrates of mixed tocopherols can be obtained from vegetable oils by treatment with chemicals. Inactive natural forms are converted to active forms **synthetically**, but are considered "natural" in the trade. Totally synthetic pure tocopherols also are commercially available.

Mixed tocopherol concentrate contain a specified minimum amount of total tocopherols, differing only in levels of the *d*-tocopherol forms. The *high-alpha* type is a recognized form of vitamin E and is also an antioxidant. The *low-alpha* type contins more of the beta, gamma and delta forms of tocopherol and is not a vitamin but is an antioxidant. Both types may contain added vegetable oil to adjust the amount of total tocopherols.

d-a-tocopherol is a red, nearly odorless, viscous oil. Oxidizes and darkens slowly in air and on exposure to light. Insoluble in water, soluble in alcohol, and miscible with acetone, ether, and vegetable oils. Mixed tocopherols concentrate occurs as a brownish red to red, clear viscous oil with a mild, characteristic odor and taste. It oxidizes and darkens slowly in air and light. Same solubility as *d*-a-tocopherol.

antioxidant for all food products. Dietary supplement.
Natural preservative; delays onset of oxidative rancidity.

BHA, BHT, TBHQ are synthetic alternatives. Rosemary extract may be an organic alternative.

12. A ''Petition Justification Statement'' which provides justification for any of the following actions requested in the petition:

A. Inclusion of a Synthetic on the National List, §§ 205.609 and 205.611

• Explain why the synthetic substance is necessary for the production or handling of an organic product.

To prevent the oxidation of fish oil and other lipids in feeds for aquatic animals. In addition, the use of some effective form of anti-oxidation is mandatory for shipping due to the danger of fire caused by the rapid oxidation of polyunsaturated fats in fish meal.

• Describe any non-synthetic substances, synthetic substances on the National List or alternative cultural methods that could be used in place of the petitioned synthetic substance.

Rosemary extracts are valuable anti-oxidants. However, Rosemary imparts an undesirable taste to fish. As a result, they can only be used in small amounts.

In conventional aquaculture, antioxidants added to lipids and feeds to prevent oxidation by reacting with free radicals are phenolics, such as butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA), and amines, such as ethoxyquin (Thorisson et al. 1992). BHA and BHT are added to feeds at a level of 0.1%, while ethoxyquin is added at 0.015%. Other antioxidants in use include dilaury l thiodi propionate, propyl gallate, and thiodipropionate. Probably the most widely used antioxidant in fish feed is ethoxyquin.

In a rancidity test, J.K. Kaitaranta in the paper in the Journal of the American Oil Chemists' Society, 1992, cited in #11 above, reports "α-Tocopherol acetate and ascorbyl palmitate showed the lowest antioxidative effects among the group of seven chemicals. Anoxomer, a synthetic phenolic polymer, had an antioxidative power comparable to that of ethoxyquin, butylated hydroxytoluene or butylated hydroxyanisole when all were applied to the oil in the concentration of 0.02%. However, the most powerful antioxidant was tertiary-butylhydroquinone (TBHQ), with an antioxidant efficiency twice that of the above-mentioned phenolic compounds when used at only 0.01% concentration in the oil. Although TBHQ and Anoxomer proved to be potential compounds for preventing rancidity in fish oils, their use is still hindered by the limited acceptance from the appropriate authorities.

Other antioxidants that delay oxidation by chelating metallic pro-oxidants include ethylenediaminetetraacetic acid (EDTA).

Many plant sources of lipidscontain naturally occurring antioxidants, mainly tocopherols. These compounds inhibit autoxidation of lipids until they are used up, at which time the rate of oxidation reactions increases very rapidly. The period of time during which antioxidants prevent oxidation is called the induction time. Chemical tests to detect lipid oxidation, such as peroxide values and TBARS, cannot measure induction time, and low values from these tests can give a false sense of security to a feed company. By testing a lipid source or feed before and after an accelerated oxidation test, such as the Shall oven test, the induction time can be estimated, and appropriate precautions taken to avoid oxidation.

Since antioxidants are mandatory for shipping fish meal in order to prevent dangerous fires, tocopherols from grain oils for organic production are preferable to BHT, BHA, ethoxyquin, EDTA and other synthetic substances described above.

• Describe the beneficial effects to the environment, human health, or farm ecosystem from use of the synthetic substance that support its use instead of the use of a non-synthetic substance or alternative cultural methods.

There are no non-synthetic anti-oxidation substances available for use as feed ingredients for aquatic animals. Tocopherols are a natural substance extracted from grains. There are several synthetic substances, such as ethoxyquin used in conventional aquaculture and livestock production.

13. A "Confidential Business Information Statement" that describes the specific required information contained in the petition that is considered to be confidential business information or confidential commercial information and the basis for that determination.

This petition does not contain any confidential business information.

Conclusions

Tocopherols and anti-oxidants are essential for the healthy production of aquatic animals. They are safe, provide no environmental risks, and there are no natural alternatives.

Previous actions by NOSB and NOP have determined that tocopherols are allowed as:

§ 205.603 Synthetic substances allowed for use in organic livestock production.
(d) As feed additives.
(3) Vitamins, used for enrichment or fortification when FDA approved.

and

§ 205.605 Nonagricultural (nonorganic) substances allowed as ingredients in or on processed products labeled as "organic" or "made with organic (specified ingredients or food group(s)).
(b) Synthetics allowed:
Tocopherols—derived from vegetable oil when rosemary extracts are not a suitable alternative.

This petition is a request for NOSB and NOP to allow tocopherols in the organic production of aquatic animals in:

"§ 205.611 Synthetic substances allowed in organic aquatic animal production
(*x*) Tocopherols."

This petition seeks a similar allowance for tocopherols for a feed ingredient for aquatic animals.

Aquaculture Working Group
George S. Lockwood, Chair

Appendix A

ADM

Material Safety Data Sheet

NFPA	WHMIS	Personal Protective Equipment	Transport Symbol
			

Preparation Date 14-Jul-2009 **Revision Date:** 14-Jul-2009 **Revision Number** 0

1. PRODUCT AND COMPANY IDENTIFICATION

Product Name: Decanox™ MTS-90 G

Product Code: 400406

Synonyms:
Tocopherols

Use of the Substance / Preparation:
Food additive Nutrient

Contact Manufacturer:
Archer Daniels Midland Company
4666 Faries Parkway
Decatur, IL 62526, USA
Telephone Number: 217 424-5200

Emergency Telephone Number:
Chemtrec 1-800-424-9300

2. HAZARDS IDENTIFICATION

Emergency Overview

The product contains no substances which at their given concentration, are considered to be hazardous to health

Appearance Light brown to Red **Physical State** Viscous liquid **Odor** Vegetable oil

Potential Health Effects

Principle Routes of Exposure	Eye contact, Skin contact, Inhalation, Ingestion.
Acute Effects	
Eyes	Contact with eyes may cause irritation.
Skin	Health injuries are not known or expected under normal use.
Inhalation	Inhalation of aerosol may cause irritation to respiratory tract.
Ingestion	Health injuries are not known or expected under normal use.
Chronic Effects	None known.
Aggravated Medical Conditions	None known.
Potential Environmental Effects	There is no known ecological information for this product
Toxicological information	See Section 11 for additional toxicological information.

3. COMPOSITION/INFORMATION ON INGREDIENTS

Common Name Mixed Tocopherols

Non-hazardous Components

Chemical Name	CAS-No	Weight %	North American Hazard Indicator
Mixed Tocopherols	1406-66-2	100	-

4. FIRST AID MEASURES

Eye Contact Rinse thoroughly with plenty of water, also under the eyelids. If eye irritation persists, consult a specialist.
Skin Contact Rinse with water
Inhalation Move to fresh air
Ingestion Immediate medical attention is not required.
Notes to Physician Treat symptomatically

5. FIRE-FIGHTING MEASURES

Flammable Properties The product is capable of burning but not readily ignited.
Suitable Extinguishing Media Water. Carbon dioxide (CO_2). Foam. Dry powder. Use extinguishing measures that are appropriate to local circumstances and the surrounding environment.
Unsuitable Extinguishing Media Do not use a solid water stream as it may scatter and spread fire.
Hazardous Combustion Products Carbon monoxide (CO), Carbon dioxide (CO_2).
Explosion Data
Sensitivity to mechanical impact No
Sensitivity to static discharge No
Specific Hazards Arising from the Chemical None known.

Protective Equipment and Precautions for Firefighters As in any fire, wear self-contained breathing apparatus pressure-demand, MSHA/NIOSH (approved or equivalent) and full protective gear.

NFPA

Health 0 **Stability and Reactivity** 0
Flammability 1 **Physical hazard** -

6. ACCIDENTAL RELEASE MEASURES

Personal Precautions Material can create slippery conditions.
Environmental Precautions Prevent further leakage or spillage if safe to do so.
Methods for Clean-up Soak up with inert absorbent material.

7. HANDLING AND STORAGE

Handling	Handle in accordance with good industrial hygiene and safety practice.
Storage	To maintain product quality, do not store in heat or direct sunlight. Keep containers dry and tightly closed to avoid moisture absorption and contamination. Keep at temperatures between 39-90° F / 4-32°C.

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

Exposure Limits
This product is not known to contain any hazardous materials with occupational exposure limits established by the region specific regulatory bodies.

Engineering Measures	Ensure adequate ventilation, especially in confined areas

Personal Protective Equipment

Eye/face Protection	Safety glasses with side-shields, if needed.
Skin and Body Protection	Protective gloves, if needed.
Respiratory Protection	No personal respiratory protective equipment normally required. In case of mist, spray or aerosol exposure wear suitable personal respiratory protection.

General Hygiene Considerations	Handle in accordance with good industrial hygiene and safety practice

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance	Light brown to Red	**Physical State**	Viscous liquid
Odor	Vegetable oil	**Odor Threshold**	Not applicable
Flash Point	> 200°C / 392°F	**Autoignition Temperature**	No information available
Boiling point	> 200°C / 392°F	**Melting/Freezing Point**	No information available
Flammability Limits in Air	No information available	**Explosion Limits**	No information available
pH	No information available	**Vapor Pressure**	No information available
Water Solubility	Insoluble	**Specific Gravity**	0.93 @ 25 °C (77 °F)
Evaporation Rate	No information available	**Vapor Density**	No information available

10. STABILITY AND REACTIVITY

Chemical Stability	Stable.
Conditions to Avoid	None known.
Incompatible Materials	Strong oxidizing agents. Alkali.
Hazardous Decomposition Products	No information available.
Possibility of Hazardous Reactions	Hazardous polymerization does not occur.

11. TOXICOLOGICAL INFORMATION

Acute Toxicity

Product Information
LD50 Oral: No information available
LD50 Dermal: No information available
LC50 Inhalation: No information available

Toxicology data for the components
No information available
Chronic Effects
Carcinogenicity
There are no known carcinogenic chemicals in this product.
OSHA: (Occupational Safety & Health Administration)
Not Listed
ACGIH: (American Conference of Governmental Industrial Hygienists)
Not Listed
NTP: (National Toxicity Program)
Not Listed
Mexico: (Official Mexican Norm NOM-010-STPS-1999)
Not Listed
IARC: (International Agency for Research on Cancer)
Not Listed

Subchronic Toxicity	No information available.	**Irritation**	No information available.
Corrosivity	No information available.	**Sensitization**	No information available.
Neurological Effects	No information available.	**Mutagenic Effects**	No information available.
Reproductive Effects	No information available.	**Developmental Effects**	No information available.
Teratogenicity	No information available.	**Target Organ Effects**	No information available.

12. ECOLOGICAL INFORMATION

Ecotoxicity

Contains no substances known to be hazardous to the environment. Contains no substances known to be not degradable in waste water treatment plants..

Persistence/Degradability	Not applicable.
Bioaccumulation/ Accumulation	Not applicable.
Mobility	The product is insoluble and floats on water.

13. DISPOSAL CONSIDERATIONS

Waste Disposal Methods	Dispose of in compliance with the laws and regulations pertaining to this product in your jurisdiction
Contaminated Packaging	Empty containers should be taken for local recycling, recovery or waste disposal

14. TRANSPORT INFORMATION

Domestic transport regulations (USA)
DOT Not regulated

Domestic transport regulations (Canada)
TDG Not regulated

Domestic transport regulations (Mexico)
MEX Not regulated

International transport regulations
ICAO Not regulated

IATA Not regulated

IMDG/IMO Not regulated

15. REGULATORY INFORMATION

International Inventories
The components of this product are reported in the following inventories:

Chemical Name	TSCA	DSL	NDSL	EINECS	ELINCS	AICS	ENCS	CHINA	PICCS	KECL	NZLoC
Mixed Tocopherols	Yes 119-13-1 54-28-4 59-02-9 148-03-8	Yes 119-13-1 54-28-4 59-02-9 148-03-8	No	Yes 204-299-01 200-201-5 200-412-2 205-708-5	No	No	Yes 9-864	Yes	Yes	Yes KE-10632 KE-10771 KE-10750 KE-10768	Yes

Legend
TSCA - Toxic Substances Control Act, Section 8(b) Inventory (USA). DSL - Domestic Substance List (Canada). NDSL - Non Domestic Substances List (Canada). EINECS - European Inventory of Existing Commercial Chemical Substances (EU). ELINCS - European List of Notified Chemical Substances (EU). AICS - Australian Inventory of Chemical Substances (Australia). ENCS - Existing and New Chemical Substances (Japan). CHINA - Chinese Inventory of Existing Chemical Substances (China). PICCS - Inventory of Chemicals and Chemical Substances (Philippines). KECL - Korean Existing and Evaluated Chemical Substances (Korea). NZLoC - New Zealand Inventory of Chemicals (New Zealand)

USA

Federal Regulations
Ozone Depleting Substances:
No Class I or Class II material is known to be used in the manufacture of, or contained, in this product.

SARA 313
Section 313 of Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA). This product is not known to contain any chemicals which are subject to the reporting requirements of the Act or regulations contained in 40 CFR 372.

SARA 311/312 Hazardous Categorization

Acute Health Hazard	No
Chronic Health Hazard	No
Fire Hazard	No
Sudden Release of Pressure Hazard	No
Reactive Hazard	No

Clean Air Act, Section 112 Hazardous Air Pollutants (HAPs) (see 40 CFR 61)
This product is not known to contain any HAPS.

State Regulations
California Proposition 65
Proposition 65 chemicals are not expected to be found in this product above those naturally present in their agricultural source.
Proposition 65 exempts naturally occurring listed chemicals from an obligation to label.

State Right-to-Know
Component Information

Chemical Name	Weight %	Illinois	Massachusetts	New Jersey	Pennsylvania	Rhode Island
Mixed Tocopherols	100	No	No	No	No	No

Canada

WHMIS Product Classification
Exempt: Food Product per Hazardous Products Act Part II Controlled Products Section 12.

WHMIS Ingredient Disclosure List IDL
No known component is listed on the WHMIS ingredients disclosure list.

(NPRI) Canadian National Pollutant Release Inventory
No known component is listed on NPRI.

This product has been classified in accordance with the hazard criteria of the Controlled Products Regulations (CPR) and the SDS contains all the information required by the CPR.

Mexico

Mexico - Grade Slight risk, Grade 1

16. OTHER INFORMATION

Prepared By Natural Health & Nutrition
Preparation Date 14-Jul-2009
Revision Date: 14-Jul-2009
Revision Summary Implementation into software system.

Disclaimer
The information provided on this (M)SDS is correct to the best of our knowledge, information and belief at the date of its publication. The information given is designed only as a guide for safe handling, use, processing, storage, transportation, disposal and release and is not to be considered as a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other material or in any process, unless specified in the text.

End of (M)SDS

Appendix B

Material Safety Data Sheet

TRADE NAME		CHEMICAL FAMILY
Naturox® IPO Liquid		Antioxidant
PROPER DOT SHIPPING NAME		DOT HAZARD CLASSIFICATION
None		N/A
MANUFACTURER		MANUFACTURER PHONE NUMBER
Kemin Industries, Inc. for Kemin Nutrisurance, Inc.		(515) 559-5100
ADDRESS		CITY/STATE/ZIP
2100 Maury Street		Des Moines, Iowa 50317

PRINCIPAL COMPONENTS	PERCENT	THRESHOLD LIMIT VALUE
Organic Sunflower Oil	N/A	N/A
Natural Mixed Tocopherols	N/A	N/A
Lecithin	N/A	N/A
Rosemary Extract	N/A	N/A

APPEARANCE & ODOR:	An amber liquid with an herbal odor		
BOILING POINT:	N/A	SOLUBILITY:	N/A
VISCOSITY:	50-150 cps at 25º C	SPECIFIC GRAVITY:	0.92 – 0.94
VAPOR DENSITY (AIR =1):	N/A PERCENT VOLATILE:	N/A	
EVAPORATION RATE (=1):	N/A REFRACTIVE INDEX	1.48 – 1.49	

FLASH POINT (TEST METHOD): (º F) Tag Closed Cup ASTM D56-79
FLAMMABLE LIMITS: LEL: N/A UEL: N/A
EXTINGUISHING MEDIA: CO_2, water
SPECIAL FIRE FIGHTING PROCEDURES: None
UNUSUAL FIRE & EXPLOSION HAZARDS: None

EYE CONTACT: Flush eyes with water at least 15 minutes. Consult a physician.
SKIN CONTACT: Wash with water.
INHALATION: Handle in well ventilated area. Remove to fresh air.
INGESTION: Consult a physician.
EMERGENCY FIRST AID: Whenever first aid is required, it should be given immediately. Prompt treatment may greatly decrease the severity of the effect.

STABILITY	Unstable.....[ ]	CONDITIONS TO AVOID:	N/A
	Stable.....[x}		
INCOMPATIBILITY:	None	MATERIALS TO AVOID:	N/A
HAZARDOUS	May Occur ....[ ]	CONDITIONS TO AVOID:	N/A
POLYMERIZATION	Not Occur.....[x]		

HAZARDOUS DECOMPOSITION PRODUCTS:
None

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Material Safety Data Sheet **Page 2**

Kemin Industries, Inc. for Kemin Nutrisurance, Inc. | Naturox® IPO Liquid | 2100 Maury St. Des Moines, IA

SPILL RESPONSE: Adjust the pH prior to appropriate disposal.
WASTE DISPOSAL: Dispose in accordance with federal, state, and local regulations.

EYE PROTECTION:
Goggles recommended.

SKIN PROTECTION:
Avoid prolonged exposure. Rubber gloves recommended.

RESPIRATORY INFORMATION:
Use of a NIOSH approved respirator is recommended if exposure may, or does exceed occupational exposure limits.

VENTILATION RECOMMENDED

No mechanical exhaust system is required.

OTHER PROTECTION:

OTHER PRECAUTIONS: Store in cool, dark place. Keep container closed when not in use.

ISSUE DATE: 16Sep08 SUPERSEDES: New

Appendix C

MEDALLION LABS

Medallion Laboratories
ANALYTICAL PROGRESS

Food Product Shelf Life

By Mark Sewald and Dr. Jon DeVries

Why Study Shelf Life?

The modern food industry has developed and expanded because of its ability to deliver a wide variety of high quality food products to consumers on a nationwide and worldwide basis. This feat has been accomplished by building stability into the products through processing, packaging, and additives that enable foods to remain fresh and wholesome throughout the distribution process. Consumer demands for convenience have fueled new innovations in the food product development, packaging and chemical industries, and the widespread desire for products to use in the microwave oven has added further impetus to this effort.

As an increasing number of new foods vie for space on supermarket shelves, the words "speed and innovation" have become the watchwords for food companies seeking to become "first to market" with successful products. That all important market share which goes to the pioneer of each successful new product keeps that company in an excellent competitive position.

Total quality is of paramount importance to this competitive posture and needs to be built into the speed and innovation system. How the consumer perceives the product is the ultimate measure of total quality. Therefore, the quality built in during the development and production process must last through the distribution and consumption stages or all is for naught.

Shelf-life studies can provide important information to product developers enabling them to ensure that the consumer will see a high quality product for a significant period of time after production. Of course long shelf-life studies do not fit with the speed requirement and therefore accelerated studies have been developed as part of innovation.

As the mechanisms of food deterioration became known to food scientists, methods of counteracting these losses in quality have been developed. The rate at which these reactions occur, the effects of temperature, water, and the myriad of other parameters have become characterized factors contributing to the science of accelerated shelf-life studies.

Processed Food Deterioration

The principal mechanisms involved in the deterioration of processed foods are as follows:

1. Microbiological spoilage sometimes accompanied by pathogen development.
2. Chemical and enzymatic activity causing lipid breakdown, color, odor, flavor, and texture changes.
3. Moisture and/or other vapor migration producing changes in texture, water activity and flavor.

Formulation and processing variables which affect these mechanisms and which can be used to control deterioration include: (1) moisture and water activity;

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(2) pH; (3) heat treatments; (4) emulsifier systems; (5) preservatives and additives; and (6) packaging.

The Importance of Moisture and Water Activity

Water has been called the universal solvent because it is a requirement for growth and metabolism of microbes, and the support of many chemical reactions which occur in food products. Water occurs in food systems in both the free and bound states. Free water is just that, free for chemical reactions, to support microbiological growth, and to act as a transporting medium for compounds. In the bound state, water is not available to participate in these reactions as it is tied up by water-soluble compounds such as sugar, salt, gums, etc., (osmotic binding) and by the surface effects of the substrate (matrix binding). These water-binding effects reduce the vapor pressure of the water over the food substrate according to Raoult's Law. By comparing this vapor pressure with that of pure water at the same temperature, one establishes a ratio which is called water activity (a_w) which by definition is 1 for pure water. A one molal solution of sugar has a a_w of 0.98, and one molal sodium chloride has a a_w of 0.9669. A saturated sodium chloride solution has a a_w of 0.755. Thus the NaC1 solution in a closed container will develop an equilibrium relative humidity (ERH) in the headspace of 75.5%.
Therefore: $a_w = ERH/100$

The ERH of a food product is defined as that relative humidity of the air surrounding the food at which the product neither gains nor loses its natural moisture; that is, it is in equilibrium with its environment. At a relative humidity above the ERH, the product will gain moisture and at a humidity below that level, it will lose moisture. A food with a a_w of 0.6 will lose moisture at a relative humidity below 60% and gain moisture above 60%.

The ERH is a valuable tool for food product and packaging development as it is an indicator of what chemical reactions may occur during distribution and of how much packaging protection should be designed for the product to give it the required shelf life. Without the protection of a package, the moisture of any food changes in direct proportion to the relative humidity. The rate at which the gain or loss of moisture occurs depends on the makeup of the product, i.e., its hygroscopicity,

absorbing moisture from the air

the temperature and the atmospheric pressure. In packaged products the changes are relatively slow, but at times a significant change can occur within a short period of time. Have you ever eaten soggy potato chips at a picnic on a hot and humid day? Have you ever received moisture test results from the lab that you were convinced were incorrect? If so, perhaps the samples were not properly packaged for transit.

Equilibrium Moisture Conditions

When a food is exposed to a constant humidity, it will equilibrate at a final moisture content called its equilibrium moisture. By exposing the product to a wide range of relative humidities, one can develop what is called a micro moisture equilibrium curve. This test is accomplished by placing a known weight of the product in a metal dish inside of a glass jar containing a saturated salt solution. Various saturated salt solutions equilibrate at certain relative humidities. The sample dishes are weighed back at various times until they reach equilibrium. The moisture value is then calculated and the texture of the sample is noted for reference. Two examples are shown in Tables 1 and 2.

Breakfast Cereal

Initial Conditions2.5%

%RH	%H2O	Texture
0.0	1.54	Crisp
11.1	2.27	Crisp
22.9	3.18	Crisp
32.9	4.59	Soft
43.9	6.55	Soggy
53.5	8.27	Soggy
64.8	11.43	Rubbery
75.5	15.88	Moldy
86.5	23.69	Moldy

Table 1: The Effect of Relative Humidity on Moisture Content And Texture of Cereal

An equilibrium moisture curve is obtained when the product equilibrium moisture (Y-axis) is plotted against the RH (X-axis). If the RH is divided by 100 to

Testing Equilibrium Moisture Effects

Food products may lose quality if the moisture level changes from the equilibrium moisture in the distribution chain. The rate of moisture change can be monitored by changes in package weight which occur during storage in appropriate temperature and humidity environments. Medallion Laboratories has computerized this old technique and applied it to a wide variety of food products. For products that suffer quality losses in high humidities, the packages are stored in what is known as the "weather room". This room is kept at constant 65% RH with temperature cycling on a day/night basis between 90°F and 74°F. These conditions are used to simulate the hot, humid summers of the southeastern United States. The packages are weighed back at weekly intervals and the gain in weight, along with the original moisture determination, are then used to calculate the moisture changes. From the moisture sorption curve developed for the product and knowledge of the package material water vapor transmission rate (WVTR), a calculation can be made to determine its shelf life.

It is difficult to obtain reliable weight change data on packages at relative humidities above 75%. Most food packages contain paper or paperboard which gain and lose moisture in the same manner as food products. When stored at a relative humidity above 75%, the amount of water gained for the paper component with a small change in humidity is large and moisture condensation also becomes a problem.

The package weight method is ideal for comparing variations where only small differences are expected. This method has been able to show moisture changes due to a few pinhole leaks in impermeable pouches.

To obtain reliable results, there are some prerequisites:

1. Initial product moistures must all be the same in each set.
2. Sealed empty packages must be used as controls.
3. The heat and humidity at the storage conditions should not result in weight changes other than from moisture, i.e., no chemical changes in leavening systems.
4. The weight variation of the packages must be small with respect to net product weight. A rule of thumb is that the weight difference between the heaviest and lightest empty packages divided by the average net weight of the product must equal 0.025 or less.

If moisture gain or loss is extremely important to the packaged food product, this method may be able to help you with shelf life questions.

MICROBIOLOGY AND THE SHELF LIFE OF REFRIGERATED PRODUCTS

Shelf life of food products is most familiar to consumers through the open dating used on refrigerated goods. The shelf life of these types of products is affected, for the most part, by their microbiological status. These products pose the highest food safety risk and have the shortest shelf life because they are the most susceptible to microbiological deterioration and the possibility of the growth of pathogenic organisms. Bacteria need certain conditions for growth – namely available moisture, the proper pH, the right temperature and nutrients and time. By controlling these conditions one can prevent the growth of these organisms and extend the shelf life. Once the product has been developed utilizing a combination of the proper ingredients, pH, water activity and microbiological inhibitors, its shelf life can be determined in real time at the various temperatures, which may be encountered during storage and distribution. The growth of yeasts, mold, spoilage and pathogenic bacteria, etc., can be monitored by microbiological methods. Other noticeable reactions such as gas production, syneresis (phase separation), and changes in color or viscosity can give further indications as to what might have to be changed in the formulation or packaging to increase the shelf life. Another means of ensuring the product will have an adequate shelf life is to challenge the product with inoculi of various spoilage organisms, as well as some potentially pathogenic bacteria. This step will ensure the product will be safe for the consumer as well as aesthetically pleasing at the end of its shelf life. *Listeria monocytogenes* grows under refrigerated conditions. It is imperative that it not be present in refrigerated

products, but that it be dealt with via elimination from the plant environment to assure against its presence in the product. Microbiological shelf-life determinations can usually be accomplished in real time and are, therefore, quite accurate.

CHEMICAL DETERIORATION

Chemically based deterioration of packaged food products can be classified into three different mechanisms: (1) Oxidation of lipids; (2) Enzymatic degradation; and (3) Non-enzymatic browning. All three can occur simultaneously in food systems and are accelerated to some extent or another by increasing storage temperatures.

Lipids and Shelf Life

One of the principal methods of predicting the shelf life of processed food products is to monitor the level of lipid degradation products in foods stored at elevated temperatures. Much of the science of accelerated shelf-life estimation has involved lipid degradation reaction rates.

Fat Oxidation and Hydrolysis

Fats are composed of glycerol chemically combined as the ester of fatty acids. The fatty acids attached to the glycerol molecule can be saturated, unsaturated and polyunsaturated in any combination. Each particular fat has its own unique combination of fatty acids and, therefore, its own physical and chemical properties. Saturated fatty acids are very stable because they contain no double bonds between the carbon atoms in the chain. Unsaturated fats (fats with double bonds) are subject to a variety of reactions. Monounsaturated fatty acids have one double bond while polyunsaturates have up to six double bonds and are the least stable of the fatty acids. These double bonds are the most reactive sites on the fatty acid chain and are easily attacked by oxygen, hydrogen, and enzymes. Each of these attackers produces a different result. When hydrogen reacts with the double bond, it eliminates (saturates) the bond. This process, called hydrogenation, produces a more saturated and thus more stable fat with a higher melting point. This is an industrial process that does not occur naturally during storage.

Enzymatic Degradation Mechanisms

The lipolytic enzyme lipase reacts with triglycerides to form free fatty acids in a degradation process known as hydrolytic rancidity. Lipase enzymes cleave fatty acids from triglycerides. The fatty acids have definite detectable flavors which can render the food unacceptable. Lauric acid (C12:0) has a strong soapy flavor and is readily detectable in rancid coconut and coconut oil. As little as 0.3% lauric acid will produce this effect. This hydrolysis reaction requires either high temperature, e.g., deep fat frying with water present or lipase enzyme activity. Therefore, it is not a reaction which occurs during normal food storage unless there is lipolytic enzyme activity. With the exception of lauric acid mentioned above, low levels of free fatty acids have minimal effect on the flavor of foods. Fatty acids from domestic oils (C16:0 or higher) do not affect the flavor until they reach a level of about 2% and then they impart a bitter taste. If butter is present, the short chain fatty acid released, butyric acid, have a very strong and undesirable odor and flavor at lower levels.

The analytical determination of these free fatty acids by titration with a standard base solution (America Oil Chemists' Society, AOCS Ca 5a-40) provides a method for following the hydrolytic rancidity process in accelerated storage tests.

The free fatty acid (FFA) test is a simple acid base titration and will measure any acid present in the food and extracted with the organic solvent used. This will include acids that may have been added to the food or produced during storage by fermentation or microbiological spoilage, therefore the FFA of a fresh product needs to be known. In most situations, FFA is not a reliable measure of reactions other than hydrolysis. Some fatty acids are produced by lipid oxidation at lower temperatures, as will be discussed later, but the levels are too low to be accurately measured by this test. At higher temperatures, both oxidation and hydrolysis occur and since the FFA test does not differentiate between them, it is not a good measure of rancidity. Lipoxygenase and peroxidase enzymes react, for the most part, on the free fatty acids themselves as part of one of the modes of another fat degradation process called oxidative rancidity. In this mechanism, the enzymes catalyze oxidative reactions on unsaturated fatty acids at their double bonds starting a chain reaction process, which produces a wide variety of degradation products.

Since enzymes are very active in promoting food

product deterioration, it is important that they be destroyed during food processing. The best illustration of this phenomenon is the chemistry of oats and oat bran.

Oats differ considerably from other cereal grains in that the oat bran fraction contains a large amount of unsaturated fat and an extremely active lipid enzyme system. The oat kernel itself, at its normal moisture of 11-13%, is very stable as the fat is protected in several ways. The fat is stored in encapsulated globules which protect it from oxygen and enzyme activity. Secondly, the normal moisture of the oat is ideal as a minimum of oxidation takes place at that level. In addition, a high level of phenolic compounds are present in the oat and they act as anti-oxidants in a manner similar to BHA and BHT.

Once the oats are milled or ground without deactivating the enzymes, the fat no longer has the same degree of protection and fat hydrolysis will begin producing free fatty acids and mono and di-glycerides. These compounds do not significantly affect flavor but do affect the physical property of oats being converted to oat products and are substrates for other enzymes which do produce off-flavored compounds.

The mono and di-glycerides produced are emulsifiers and the long chain free fatty acids fit nicely into the starch helixes of oat flour. Through hydrogen bonding, a fatty acid/starch complex is formed. These inclusion compounds prevent the starch from forming a paste when mixed with water. In dilute solutions, they form a precipitate making the formation of a good oat cereal dough very difficult.

Oats also contain a powerful lipoxygenase that adds oxygen to the double bonds of unsaturated fat to form peroxides, as discussed above. The other enzyme present, peroxidase, reduces peroxides producing mono-, di-, and tri-hydroxy acids that are extremely bitter compounds. These compounds cause the bitter flavor of rancid wheat germ.

The activity of these enzymes is proportional to the amount of available water present and, therefore, to the water activity as seen in Figure 1. They are most readily destroyed by moist heat above 190°F for several minutes. Dry heat is much less effective at deactivating these enzymes in cereal systems.

In most biological systems, peroxidase requires much more heat to destroy than lipases, lipoxygenases or any of the other enzymes that may be present. It would follow then that if the peroxidase has been destroyed, the other enzymes have also been deactivated.

Cereals can be checked for proper enzyme deactivation by using a simple colorimetric procedure based on the peroxidase oxidation of a phenolic dye (2, 6-dichloroindophenol), which has been reduced to its leuco form by ascorbic acid. During the reoxidation, a blue color is formed which can be used to measure peroxidase activity. This test is an adaptation of an old U.S. Army Quartermaster Corps method used to ensure the proper blanching of vegetables.

Oxidative Rancidity Mechanisms

Hydrolytic rancidity, for all practical purposes, does not occur during low temperature storage of foods. However, the oxidative rancidity process does occur at these temperatures because it is a chemical reaction which requires much lower activation energies to initiate. Lipid oxidation and the formation of hydroperoxides occur via three different mechanisms.

1. The Free Radical Route
2. The Lipoxygenase Route (which has been discussed above)
3. The Photo-Oxidation Route

The free radical route is an oxidation reaction producing free radicals that lead to peroxides that in turn are converted to alcohols, aldehydes, ketones, and free fatty acids. Many of these compounds have very objectionable flavors and odors and are what is smelled and tasted in rancid fat. This reaction, called autoxidation or peroxidation, takes place at the double bonds of unsaturated fatty acids, principally oleic C18:1, linoleic C18:2, and linolenic C18:3. The oxidation reaction occurs 64 times faster with linoleic and 100 times faster with linolenic when compared to oleic acid.

The initial reaction or initiation step for the free radical route requires the presence of a catalyst, e.g., heat, light or high-energy radiation or metal ions, e.g., copper ions. This is followed by the propagation steps that are chain reactive or autocatalytic through formation of more free radicals. Free radicals are both initiators of and products of these propagation reactions. At some point during this propagation process, free radicals themselves combine to form products that eventually can terminate the reaction.

The third mechanism involves photo-oxidation and singlet oxygen in the formation of hydroperoxides from free fatty acids. Photosensitive compounds, e.g., riboflavin, chlorophyll, myoglobin, erythrosine, and heavy metal ions are excited to a high-energy state by absorbing light. This energy reacts with the normal triplet ground state of oxygen atoms to form a very reactive singlet oxygen atom. Singlet oxygen attacks double bonds 1500 times faster than the triplet state molecule.[1]

The process of oxidative reactions during storage studies can be followed analytically by determining the peroxide value in a fat or oil or by quantitating the aldehyde, n-hexanal, in food products.

Hydroperoxides

Most peroxides are odorless and tasteless *per se*, but they are further involved in the chain of reactions which produce the objectionable compounds. Oxidation produces a number of different types of peroxides, some fairly stable, others so unstable that one cannot measure them by the normal iodometric method for peroxide value (PV) (AOAC Official Method 965.33). Such highly unstable peroxides tend to be formed from compounds that contain conjugated double bonds (R-CH=CH-CH=CH-R) such as fish oil, vitamin A, etc. In normal fats and oils containing methylene interrupted double bonds (R-CH=CH-CH2-CH=CH-R), the peroxides formed are primarily hydroperoxides which are stable for weeks or even months at room temperature. When one monitors the rate of oxidation of a refined oil using the Oil Stability Index Method (OSI) (AOCS Cd12b), or the Active Oxygen Method (AOM), (AOCS Cd12) one can demonstrate that after the induction period, the PV increases quite rapidly. This induction period is a time during which there is little change in the peroxide value measurements (often too small to measure) and can last for some time with high stability oils. As oxidation proceeds, the rate of peroxide decomposition with respect to formation increases. Eventually the peroxide values will actually begin to decrease because the formation is slower than the decomposition. Some foods contain substances such as metal ions or enzymes that enhance the decomposition of the peroxides making the PV meaningless as a method of measuring rancidity. The PV test is most properly applied as a measure of the quality of fresh oils which should have a PV of one or less. Shortening with a PV of greater than 5 should not be used in the manufacture of mix products, as it will significantly decrease the shelf life of the product.

Aldehydes

Hydroperoxides break down to form a wide variety of decomposition products that are further oxidized and degraded. Compounds called aldehydes are one of the groups produced and can be used as a means of tracking the progress of fat degradation. The aldehyde n-hexanal can be determined at very low levels in foods using a steam driven headspace gas chromatographic technique.[2] This method has provided excellent results on low fat products such as cereals and cereal grains and is the method of choice for shelf-life studies designed to study oxidative rancidity.

THE KINETICS OF SHELF-LIFE TESTING

The prediction of shelf life for food products is based on the application of the principles of temperature dependent chemical reaction kinetics. These reaction rates, as Figure 1 depicts, depend on product composition as well as environmental factors, i.e., temperature, humidity, atmosphere, etc. Basic to any predictive use of reaction kinetics is that the relationship between the measurable changing reaction parameter and time be linear. Labuza[3] has reported that quality loss follows the equation

$$dQ/dt = k(Q_A)^n$$

where dQ/dt is the change in the measurable quality factor A, with time, k is the rate constant in appropriate units, and n is the order of the chemical reaction of the quality factor. The order of reaction for most quality attributes in food products is either zero, first or second. In zero order reactions, the rate of loss of the quality factor is constant or linear

and the resulting curve will be linear on a linear plot. First order reactions are not linear but are dependent on the amount of the quality factor that remains in the sample at the time. In these types of reactions, a linear prediction curve is constructed using semilogarithmic coordinates. Typical first order reactions are: (1) rancidity, (2) microbial growth and death, (3) microbial production products, (4) vitamin losses in dried foods, and (5) loss of protein quality.

The loss of vitamin C in liquid preparations has been called a second order reaction because it is dependent on the level of both the ascorbic acid and oxygen. Reciprocal plots are linear for these reactions.

A Case Study Example

A study of vitamin losses in cereal products provides a practical example of the value of shelf life studies. A cereal product fortified with vitamins A and C was studied to find out what initial levels of these vitamins would need to be added in order to ensure that the product still would meet label claims after six months at 70°F/38%RH. The product was stored at both 70°F and 100°F and vitamin assays performed at intervals over a several week period. The vitamin A degradation reaction is first order which means the rate of change in the vitamin concentration is proportional to its concentration and the vitamin analytical values should be plotted as log values. A preferred method is to convert the analytical values to percent of original level of the vitamin or to a retention ratio of original versus remaining amounts. The log of this value is then plotted versus time. This makes data comparison and table or graph production simpler. A computer spreadsheet program is used to perform this function, figure the log value (fitting the data to the kinetic model), and run regression values. From this data one calculates the number of weeks required at the given conditions it would take to lose 25% of the original levels of the vitamins and make recommendations to the developers.

The results of this and similar tests, along with certain formula and product characteristics, were put into the computer for statistical analysis. The results showed that there were three different patterns of vitamin degradation in these cereal products. The common denominator for vitamin A degradation was certain formula characteristics while for vitamin C it was water activity. In addition, it was found that the vitamin A deteriorated roughly three times faster at 100°F than it did at 70°F which means it has a Q_{10} of 2. What is Q_{10} you ask?

The Concept of Q10

One of the most frequently asked questions regarding shelf-life studies has to be: "One week at 100°F equals how many weeks at room temperature?" The answer depends on the type of product and the mode of degradation involved.

Each of the chemical deterioration reactions requires a certain amount of energy to get started. This is called activation energy, measured in kcal/mol. Table 2 contains some typical values. The higher the activation energy is for a reaction, the greater the acceleration with increases in temperature. A simple way to express this acceleration is to use the Q_{10} concept. Q_{10} is the increase in the rate of the reaction when the temperature is increased by 10 degrees centigrade (18°F). For example, if a food has a stability of 20 weeks at 20°C and 10 weeks at 30°C, then the Q_{10} will be 20/10 or 2. The rate of reaction being followed is doubled for the 10°C temperature rise. This value can be calculated from the data of most storage tests where the product has been stored at two or more temperatures regardless of whether or not they are 10°C apart. Table 3 shows some relationships between weeks at 70°F and 100°F for various Q_{10} values. These temperatures are more than 10°C apart and were, therefore, derived from equations.

Reaction Activation Energy (Kcal/mol)	
Oxidative rancidity	10-25
Enzyme reactions	10-30
Vitamin losses	20-30
Non-enzymatic browning	25-50

TABLE 3: Food Deterioration Activation Energies

Cereals, which experience enzymatic fat oxidation,

have Q_{10}'s of about 2, while low fat cereals with no enzyme activity have Q_{10}'s of about 3. Tomato powder experiences non-enzymatic browning that has a high activation energy and, therefore, has a Q_{10} of 4 or more. The word "about" as used above is important as these values can vary somewhat for the same product produced on different days or in different plants. As can be seen from Table 3, a small difference in the value of Q_{10} can make a rather large difference in the shelf-life projection. For instance, a product which lasts 10 weeks at 100°F and has a Q_{10} of 1.5 would last 20 weeks at 70°F. A difference in the Q_{10} of 0.5 would shift the shelf life from 20 weeks at 70°F to 32 weeks at that temperature, a 60% difference.

Q_{10}	1 Week @100° F= This Number of Weeks@ 70° F
1.5	2.0
2.0	3.2
2.5	4.6
3.0	6.2
4.0	10.1
5.0	14.6

TABLE 3: Storage week equivalents for various Q_{10} values

TYPICAL SHELF-LIFE STUDY DESIGN

The first step in setting up a shelf-life study is to select one of the degradation reactions which are expected to occur in the product at typical storage temperatures, can be measured, and can be used as an index of quality loss. As discussed, these could include lipid oxidation, vitamin loss, gain or loss of moisture, etc. means the more accurate the analysis, the more precise the shelf-life prediction.

Here are a few guidelines for storage studies involving fat degradation.

1. ***Products with less than 2.5% fat:***

Do not run peroxide values or free fatty acids tests as the fat extraction process necessary to obtain enough fat is too rigorous and may end up producing artificially high results. The best test for these types of products would be hexanal.

2. ***Samples with 2.5% - 10% fat:***

Do not use PV or FFA. Select a fat acidity test which utilizes a Soxhlet type of extraction followed by the base titration.

3. ***Samples with more than 10% fat:***

FFA, PV, and hexanal may yield good results if the method measures the proper deterioration product. For the PV test to be effective on food products, the sample history needs to be known.

Peroxide value and free fatty acid tests are analytical methods typically used for fats and oils. If the fat must first be extracted from food products in order to run these tests, the following statements must be true to ensure valid results.

1. The fat extracted must be representative of the fat in the food.

2. No non-fat compounds, which would interfere with the test, should be extracted with the fat.

3. No active fat compounds can be either produced or destroyed during the extraction process.

4. The solvents used must be free of any active substances.

Next, select the package that you want to protect the product in the distribution channels. This will enable you to generate data more pertinent to the product's actual shelf life. Storage temperature conditions should then be chosen which fit the product and give reliable results in a reasonable amount of time. Common temperatures used would be 20, 30, 40, and 55°C (68, 86, 104, and 131°F). At least two temperatures are required with three or four preferred for more accurate predictions. A control, stored at 0°F, can also be used.

The frequency of the analytical testing is the next important decision. The higher the storage temperature, the more frequent should be the testing. Weekly tests are common for most products unless a Q_{10} is known.

Labuza[4] has developed the following equation for testing frequency:

$$F2 = f1 \times Q_{10}^{\Delta/10}$$

where f1 is the time between tests at the higher temperature, f2 at the lower temperature, and "delta" is the difference in degrees centigrade between the two. For a product with a Q_{10} of 2, tested each week at 30°C, the frequency at 20°C would be:

$f2 = 1 \times 2^{10/10}$ or $f2 = 2$ weeks

Each testing temperature should have at least six data points over time to make the study results statistically reliable.

The results should be plotted as they are developed in order to ensure the experimental design is working properly and changes can be made in the testing frequency, if necessary.
Thoroughly document all of the data so that results can be pooled with the results of a whole product line. Lessons learned can mean the next project is much simpler to design and carry out.

Further Reading

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