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OIL-DRI
CORPORATION OF AMERICA

Creating Value From Sorbent Minerals

Innovation Center

30 April 2009

Program Manager
USDA/AMS/TM/NOP
Room 4004-So.
Ag Stop 0268
1400 Independence Ave. SW
Washington, DC 20250

Dear Program Manager:

Attached in duplicate is our petition for inclusion of the mineral attapulgite (a non-synthetic, non-agricultural substance) onto the National List of Substances Allowed and Prohibited in Organic Production and Handling. We are petitioning to have attapulgite included as allowed for the applications of a bleaching earth of vegetable and animal oils and as a feed additive for the bleaching clay filter cake which is added to animal feeds as a nutritional supplement.

This petition is being submitted at the suggestion of Mr. Robert Pooler to replace the previous petition which was tabled in 1996 and cannot be found.

We appreciate your consideration of our petition.

Sincerely,

Richard V. Hardin

Richard V. Hardin

Oil-Dri Corporation of America
Innovation Center
777 Forest Edge Drive
Vernon Hills, IL 60061

Phone 847-634-3090
Fax 847-634-4595
e-mail: dick.hardin@oildri.com

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NOSB NATIONAL LIST PETITION

Attapulgite as Bleaching Earth
For
Vegetable and Animal Oils

April 30, 2009

Oil-Dri Corporation of America

Petition for Allowing Attapulgite on the National List of Substances Allowed and Prohibited in Organic Production and Handling

Item A:

Petition for non-agricultural (non-organic) substance allowed in or on processed products labeled as "organic" or "made with organic (specified ingredients)," § 205.605.

Item B:

1. Substance's common name: Attapulgite

   Other names: Fuller's Earth
   Palygorskite
   Hormite

2. Manufacturer's name and contact information:

   Oil-Dri Corporation of America
   410 N. Michigan Avenue
   Suite 400
   Chicago, IL 60611-4213
   Corporate Office Phone: 312-321-1515
   Research Center Phone: 847-634-3090
   Research Center Fax: 847-634-4595
   Contact: Dr. Marc Herpfer 847-634-3090
   Research Director

3. Current uses of substance with organic materials:

   a. Processing aid – bleaching clay for purifying vegetable and animal oils
   b. Animal feed additive – addition of filter cake from vegetable/animal oil bleaching process to animal feed for the additional nutrition of the oil

4. Livestock or handling activities for the substance:

   a. Livestock
      i. Animal feed additive. Filter cake removed from the filter presses in the vegetable/animal oil bleaching process is added to animal feed to provide additional nutrition derived from the oil absorbed on the filter cake.

b. Processing
   i. Bleaching clay. Very small particles of clay (<325 mesh) are used to remove colors, chlorophyll, and metals to enhance the purity, stability, and appearance of vegetable and animal oils. The porous clay with its active surface sites is added to the heated liquid oil (~220°F) at a level of 0.5 – 5.0% of the weight of the oil, stirred and maintained for a specified period of time (generally ~30 minutes), and filtered out of the oil, carrying the adsorbed colors, chlorophyll, metals and other undesirable substances with it.

5. <u>Source of the substance and a detailed description of its manufacturing or processing procedures from the basic component to the final product:</u>
   a. Attapulgite is a naturally occurring mineral which is a hydrated alumino-magnesium silicate with the general chemical formula $(Mg_{1-x}Al_x)_5 (Si_8O_{20}) (OH)_2 (OH_2)_4 \bullet 4H_2O$ and the general structure shown below in Figure 1:

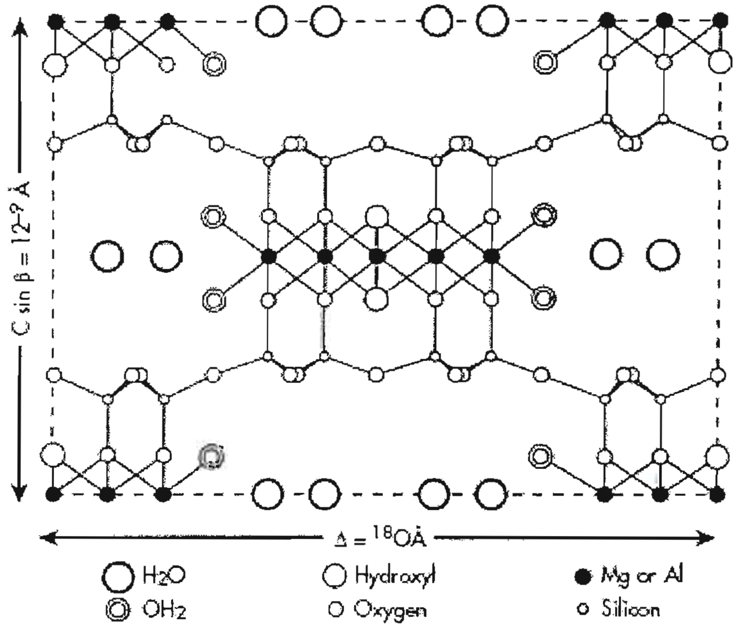

Figure 1. Structure of Attapulgite

   b. Important deposits of this mineral are found in southeastern United States, China, and Senegal, with the deposits in south Georgia – north Florida dominating the world's production. The deposits in the United States, shown in the map on the next page in Figure 2, were formed in a shallow water trough that connected the Gulf of Mexico with the Southeast Georgia Embayment on the Atlantic Ocean. The seawater in this trough was characterized by fluctuating salinities, and at times the lagoons were closed off from normal circulation. There was sufficient magnesium present to precipitate attapulgite (palygorskite). The mineralogical content changes from dominantly palygorskite in the Quincy-Attapulgus District to a mixture of smectite and palygorskite in the northern area around Ochlocknee and Meigs, Georgia.

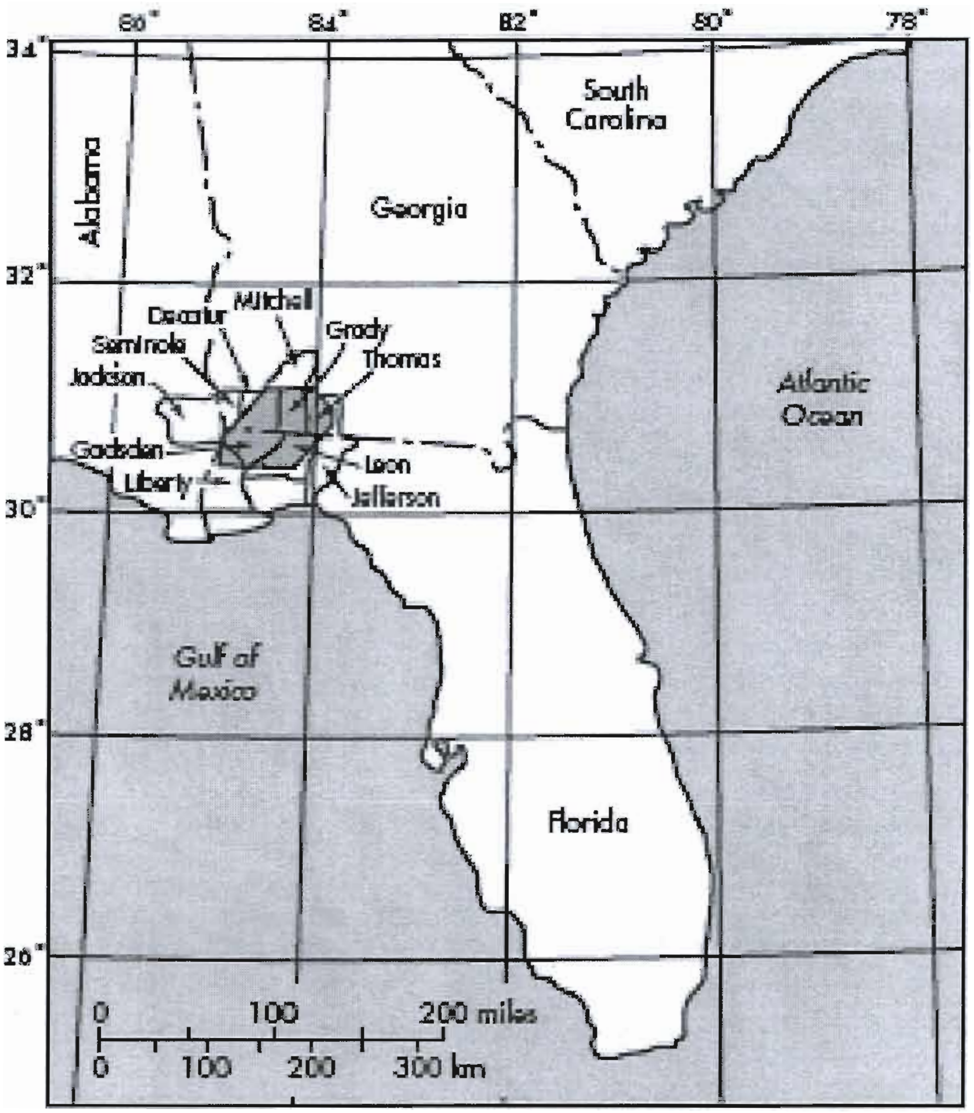

Figure 2. Location of the south Georgia-north Florida Attapulgite deposits.

c. Attapulgite is surface mined by open-pit methods. Figure 3 shows a general process flow sheet for the mining and processing of attapulgite for natural bleaching clays.

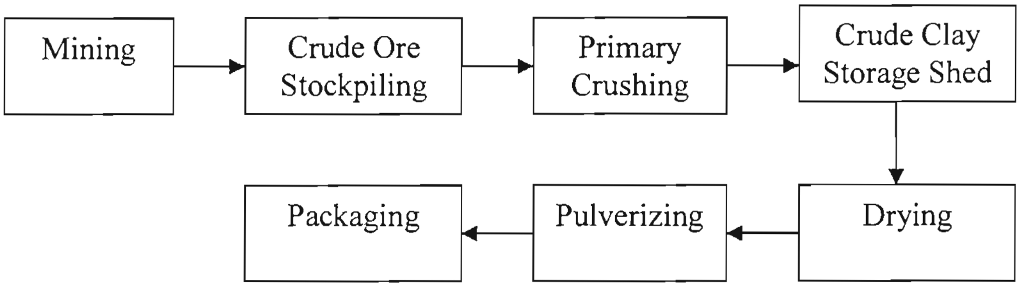

Figure 3. Process flow sheet for Attapulgite production for natural bleaching clay.

The process starts with mine planning and permitting based on core drilling on grids of 50 to 100 feet and careful clay quality testing. Overburden is stripped with motorized scrapers, draglines, shovels or bulldozers. It is backfilled into nearby previously mined-out pits where the disturbed land is restored to attractive, stable non-eroding slopes. Cover crops of pasture grass and select seedlings are planted on the reclaimed land to blend in with the original pre-mined terrain. Where possible, the land is developed into fishing ponds.

The clay is mined from the area from which the overburden has been stripped using shovels, backhoes, small draglines, or front-end loaders. It is then loaded into trucks that transport the clay to the processing plant where it is put into a raw clay stockpile, run through a primary crusher, and stored in the crude clay shed. The actual processing is generally quite simple, involving heating, milling, screening, and packaging in various combinations, depending upon the product required.

Natural bleaching clay is a fine powder product that is produced by the following steps:

   i. The shredded clay from the crude clay shed is dried in a rotary dryer and pulverized in a Raymond mill. As an optional method, the shredded clay from the crude clay shed can be dried and pulverized simultaneously in a heated hammer mill such as a Williams mill.
   ii. The dried, pulverized clay is packaged or put into bulk containers for transport to the customer.

6. <u>Summary of any available previous reviews by State or private certification programs or other organizations of the petitioned substance:</u>
   a. Natural Bleaching Earth
      i. Coleman, Eugene C., Director Division of Petition Control, Center for Food Safety and Applied Nutrition, Department of Health & Human Services, FDA, letter of July 9, 1993, confirming the

        acceptability of using Fuller's Earth for the processing of edible oils. (Exhibit 5)
    ii. Chaudry, Muhammad Munir, Ph.D., Halal Administrator, The Islamic Food and Nutrition Council of America, IFANCA HALAL Product Certificate, September 4, 2008, certifying that Pure Flo B-80 natural bleaching earth is Halal for use into the Halal products. (Exhibit 6)
    iii. Genack, Rabbi Menachem, Rabbinic Administrator, CEO, Orthodox Union Letter of Certification, December 1, 2008, certifying that Pure Flo B-80 is kosher for Passover and year-round use. (Exhibit 7)
    iv. Starling, Bill, Inspector, The Symbol Scheme Soil Association, letter of April 7, 1997, confirming that Pure Flo B-80 is certified as a processing aid in organic food processing. (Exhibit 8)
    v. Commission Directive 2001/30/EC, May 2, 2001, listing bentonite natural clays as an additive in foodstuffs intended for human consumption. (Exhibit 9)
  b. Feed additive
    i. Table 87.5 Additional Special Purpose Products, 2008 Official Publication, Association of American Feed Control Officials Incorporated, page 345, confirming the acceptability of attapulgite for use as a feed additive. (Exhibit 10)
    ii. Regulation (EC) No. 1831/2003, Community Register of Feed Additives Rev.48, April 23, 2009, authorizing use of attapulgite and bentonite-montmorillonite as a feed additive. (Exhibit 11)
    iii. Feeds Regulations 1983, Canadian Food Inspection Agency, September 19, 2007, listing attapulgite as a feed additive. (Exhibit 12)
    iv. OMRI Products List 2007, certifying bentonite type clays as acceptable as an additive and a processing aid for animal feeds, p. 18. (Exhibit 13)
    v. 7 C.F.R. §205.605 certifying bentonite type clays as allowed as ingredients in or on processed products labeled as "organic" or "made with organic ingredients. (Exhibit 14)
    vi. International Journal of Toxicology, 2003; 22 Suppl 1:37-102, The Cosmetic Ingredient Review Expert Panel concluded that attapulgite is safe (from the standpoint of its fiber length) as currently used in cosmetic formulations. (Exhibit 15)

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

  a. Substance is generally recognized as safe – Title 21 CFR Part 582.1., 6 pages. (Exhibit 16)
  b. Substance is generally recognized as safe (GRAS) for indirect food substance – CFR Part 582.

8. The Chemical Abstract Service (CAS) number or other product numbers of the substance and labels of products that contain the petitioned substance:
    a. CAS # for Attapulgite – 12174-11-7
    b. CAS # for Fuller's Earth – 8031-18-3
    c. CAS # for Clay – 1302-78-9
    d. Substance is sold by the petitioner under the label Pure Flo® B-80 bleaching earth

9. The substance's physical properties and chemical mode of action including:
    a. Chemical interactions with other substances, especially substances used in organic production:
        i. Bleaching clay. Attapulgite has an extensive system of channels and porosity whose active surface area sites remove (adsorb) undesirable color, metals, odor and other unwanted substances in vegetable and animal oils.

    b. Toxicity and environmental persistence:
        i. Attapulgite is a naturally occurring clay substance and has no overt toxic or environmental effects.

    c. Environmental impacts from its use and/or manufacture:
        i. The manufacturing of attapulgite falls under and conforms to the strict guidelines of the Mine Safety and Health Administration. All mining activity falls under EPA Title 5 for air, water, mine, and wetlands permits. All mined areas are returned to their natural state. The surface is leveled or sloped to meet the standards prescribed by the government, and grasses and /or trees are planted. Where possible, fishing ponds are created.
        ii. The major environmental issue with manufacturing is air quality because of dust. Dust collectors are used on dryers, pulverizers, baggers and conveyor transport points.

    d. Effects on human health:
        i. Exposure to excessive amounts of attapulgite dust, as with any dust, should be avoided. The use of dust collectors, face masks, and other devices protects workers from inhaling too much dust.
        ii. Attapulgite, like most clays, contains quartz which is a crystalline silica. IARC, in Monograph 68, has concluded that crystalline silica inhaled in the form of quartz from occupational sources is carcinogenic to humans (Group 1). Carcinogenicity, however, was not detected in all industrial circumstances studied. Adverse effects to human health would not be expected from normal use of this product because:
            - Applications and exposure data indicate that exposure to respirable quartz in the bleaching clay product with normal

        use is well below the OSHA Permissible Exposure Limit and ACGIH Threshold Limit Value
    - The petitioner is not aware of any scientific or medical data available indicating that exposure to dust from the bleaching clay under conditions of normal use will cause silicosis or cancer
  - iii. Attapulgite contains no deleterious trace elements or chemical compounds at levels that are hazardous to human health.

- e. Effects on soil organisms, crop, or livestock:
  - i. Attapulgite, being a natural material, should have no deleterious effect on soil organisms, crops, or livestock.

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:
    - a. Petitioner's MSDS # 5001000 for B-80 bleaching earth is attached as Exhibit 1.
    - b. No substance report on attapulgite is available from the National Institute of Environmental Health Studies (Sciences)

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:

    (See Exhibits 2 & 3)

12. A "Petition Justification Statement" which provides justification for "Inclusion of a Non-Synthetic, Non-Agricultural Substance onto the National List, §205.605(a):"

    (See Exhibit 4)

13. A confidential Business Information Statement which describes the specific required information contained in the petition that is considered to be Confidential Business Information (CBI) or confidential commercial information and the basis for that determination:

    - a. No information provided in this petition is considered to be Confidential Business Information (CBI).

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Exhibit 1

OIL·DRI
CORPORATION OF AMERICA
410 North Michigan Avenue
Chicago, IL 60611

Material Safety Data Sheet

PURE-FLO® B-80 bleaching clay (#5001000)

☎ (312)321-1515, Information (800)424-9300, Emergency

1. PRODUCT IDENTIFICATION

MSDS Number:	5001000
Identity:	PURE-FLO® B-80 bleaching clay
Issued:	February 23, 2009
Chemical Name	Fullers Earth and/or Montmorillonite Clay

2. COMPOSITION

Component	CAS Number	Amount
Montmorillonite Clay and/or Fullers Earth	1302-78-9 / 8031-18-3	85-100%
Quartz	14808-60-7	0-10%

3. HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW

This product is a non-combustible, chemically inert mineral. This mineral sample contains a small amount of naturally-occurring crystalline silica as quartz. Prolonged overexposure to respirable crystalline silica may cause lung disease (silicosis). IARC, in Monograph 68, has concluded that crystalline silica inhaled in the form of quartz from occupational sources is carcinogenic to humans (Group 1); however, carcinogenicity was not detected in all industrial circumstances studied. Because applications and exposure data indicate that exposure to respirable quartz in this product with normal use is well below the OSHA Permissible Exposure Limit (PEL) and ACGIH Threshold Limit Value (TLV); and because the company is not aware of any scientific or medical data available indicating that exposure to dust from this product under conditions of normal use will cause silicosis or cancer; adverse effects would not be expected from normal use of this product.

HEALTH HAZARDS

INGESTION:	No adverse effects expected with unused material.
INHALATION:	Inhalation of excessive concentrations of dust may cause irritation of mucous membranes and upper respiratory tract.
EYE:	Contact may cause mechanical irritation and possible injury.
SKIN:	No adverse effects expected.
SENSITIZATION:	No adverse effects expected.

CHRONIC/CARCINOGENICITY:

Inhalation of excessive concentrations of any dust, including this material, may lead to lung injury. This product contains crystalline silica. Excessive inhalation of respirable crystalline silica may cause silicosis, a progressive, disabling and fatal disease of the lung. Symptoms may include cough, shortness of breath, wheezing and reduced pulmonary function. The International Agency for Research on Cancer (IARC), in Monograph 68 has concluded that crystalline silica inhaled in the form of quartz or cristobalite, from occupational sources is carcinogenic to humans (Group 1). However, in making the overall evaluation, the Working Group noted that carcinogenicity was not detected in all industrial circumstances studied.

Carcinogenicity may be dependent on inherent characteristics of the crystalline silica or on external factors affecting its biological activity or distribution of its polymorphs. The National Toxicology Program (NTP) classifies crystalline silica as a known carcinogen. Because applications and exposure data indicate that exposure to respirable quartz in this product with normal use is well below the OSHA Permissible Exposure Limit (PEL) and ACGIH Threshold Limit Value (TLV); and because the company is not aware of any scientific or medical data available indicating that exposure to dust from this product under conditions of normal use will cause silicosis or cancer; adverse effects would not be expected from normal use of this product.

MEDICAL CONDITIONS AGGRAVATED BY EXPOSURE:

None currently known.

4. FIRST AID MEASURES

EYE: Immediately flush eyes with cool running water, lifting upper and lower lids. If irritation persists or for foreign body in the eye, get immediate medical attention.

SKIN: None needed for normal use.

INGESTION: If large amount of unused material is swallowed, get medical attention.

INHALATION: Remove to fresh air.

5. FIREFIGHTING MEASURES

FLASH POINT: This product is not combustible.

FLAMMABLE LIMITS Not applicable

EXTINGUISHING MEDIA:

Use media that is appropriate for surrounding fire.

UNUSUAL FIRE OR EXPLOSION HAZARDS:

None

SPECIAL FIREFIGHTING INSTRUCTIONS

None required.

HAZARDOUS COMBUSTION PRODUCTS:

None

6. ACCIDENTAL RELEASE MEASURES

Sweep up and collect for re-use or disposal

7. HANDLING AND STORAGE

HANDLING: Avoid breathing dust. If clothing becomes dusty, launder before re-use.

STORAGE: Store in a dry area.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

EXPOSURE GUIDELINES:

Component	Exposure Limit
Montmorillonite Clay and/or Fullers Earth	PEL - 15 mg/m^3 TWA (total dust) PEL - 5 mg/m^3 TWA (respirable fraction)
Quartz	PEL - 10 mg/m^3/%SiO_2+2 TWA TLV - 0.025 mg/m^3 TWA

PEL- OSHA Permissable Exposure Limit. TLV- American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value. TWA- 8 hour Weighted Average. STEL-Short Term Exposure Limit.

ENGINEERING CONTROLS:
For operations where the exposure limit may be exceeded, local exhaust ventilation is recommended.

RESPIRATORY PROTECTION:
For operations where the exposure limit may be exceeded, a NIOSH/MSHA approved high efficiency particulate respirator is recommended.

SKIN PROTECTION: None required for normal use.

EYE PROTECTION: Safety glasses or goggles recommended.

OTHER: None required for normal use.

9. PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE AND ODOR:
Gray to tan powder, odorless

PHYSICAL STATE: Solid

BOILING POINT: Not applicable

VAPOR PRESSURE: Not applicable

VAPOR DENSITY: Not applicable

SOLUBILITY IN WATER:
Insoluble

SPECIFIC GRAVITY: 2.2

pH: <7.8

MELTING POINT: Not applicable

OCTANOL/WATER COEFFICIENT:
Not available

10. STABILITY AND REACTIVITY

STABILITY: Stable

INCOMPATIBILITY: Physical contact between this material and turpentine, hydrofluoric acid, vegetable oil or other unsaturated organic compounds (such as fish oil) may generate heat and/or fire. Do not use this material with these compounds.

HAZARDOUS DECOMPOSITION PRODUCTS

None

HAZARDOUS POLYMERIZATION:

Will not occur.

11. TOXICOLOGICAL INFORMATION

No data available.

12. ECOLOGICAL INFORMATION

No data available.

13. DISPOSAL CONSIDERATIONS

Unused material is suitable for disposal in sanitary landfill. Without proper precautions, spent bleaching clay used in bleaching fats and edible oils is known to spontaneously combust. Procedures for handling spent clay follow: Landfills: To suppress spontaneous combustion, heat can be dissipated by spreading out the clay and/or spraying with water. Cover spent clay with non-combustibles. Plant Use: When purging the filter cake of excess oil before cleaning the filter press, excessive blowing with air can cause spontaneous combustion. To eliminate this risk, either use nitrogen or limit blowing with air. When purging the filter cake with steam, it is recommended that you not follow the steam purging with air blowing.

14. TRANSPORT INFORMATION

PROPER SHIPPING NAME:

Not regulated

UN NUMBER: Not applicable

HAZARD CLASS/PACKING GROUP:

Not applicable

LABELS REQUIRED: None

15. REGULATORY INFORMATION

CERCLA/SUPERFUND None

SARA HAZARD CATEGORY (311/312):

Chronic Health

SARA 313: None

TSCA: All of the components of this product are listed on the EPA TSCA Inventory or exempt from notification requirements.

EINECS: All of the components of this product are listed on the EINECS Inventory or exempt from notification requirements

EEC R&S Phrases: Xn Harmful, R48/20 Harmful: Danger of serious damage to health by prolonged exposure by inhalation; S22 Do not breath dust; S38 In case of insufficient ventilation, wear suitable respiratory equipment.

JAPAN MITI:	All of the components of this product are existing chemical substances as defined in the Chemical Substances Control Law.
AICS:	All of the components of this product are listed on the AICS Inventory or exempt from notification requirements
CANADIAN DSL:	All of the components of this product are listed on the Canadian Domestic Substance List or exempt from notification requirements.
CA PROPOSITION 65:	This product contains respirable crystalline silica which is known to the State of California to cause cancer.

16. OTHER INFORMATION

NFPA RATING:	Health=1 Fire=0 Reactivity=0
HMIS RATING:	Health=1* Fire=0 Reactivity=0

The information in this data sheet is believed to be accurate. However, each purchaser should make its own test to determine the suitability of the product for its purposes. OIL-DRI CORPORATION OF AMERICA MAKES NO WARRANTY, EXPRESSED OR IMPLIED, WITH RESPECT TO THE PRODUCT and assumes no responsibility for any risk or liability arising from the use of the information or the product. Statements about the product should not be construed as recommendations to use the product in infringement of any patent.

APPENDIX. ASSOCIATED PRODUCTS

This MSDS applies to the following products:

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Exhibit 2

Research Information regarding Attapulgite as a Bleaching Earth

Bleaching earths are clays, usually consisting of smectite minerals that have found use for approximately one hundred years for improving the quality of vegetable and animal oils. The edible oil industry world-wide largely is dependent on them (Patterson 1992). Until approximately 20 years ago, successful bleaching earths resulted from the activation of naturally-occurring smectite minerals by acid. This procedure consisted of heating the smectite minerals in a strong acid solution, then filtering and washing, followed by drying and pulverization (Exhibit 17: Patterson 1992, p.79; Exhibit 18: Zschau 2000, pp. 159 & 423). The activated bleaching earth, having experienced this severe acid treatment, no longer is a naturally-occurring substance.

In the mid 1980's, Oil-Dri Corporation of America discovered a natural earth material that could successfully compete with the acid-activated bleaching earths. This natural earth is a naturally-occurring fullers earth (attapulgite type) that consists of an intimate association of smectite and hormite minerals. Brooks (Exhibit 19) showed how this type of natural bleaching earth could bleach oils successfully under the conditions of the California Organic Foods Act of 1990.

Oil-Dri Corporation over the ensuing years has made numerous presentations, and published numerous papers in the trade and scientific literature of the efficacy. In particular, Brooks (Exhibit 20) showed that a natural fullers earth bleaching earth reduced the amount of free fatty acids encountered during the bleaching process and increased the oil yield. Yoo and Lin (Exhibit 21) showed that for natural bleaching earths, adsorption of chlorophyll correlated well with the pore volume of the bleaching earth.

No research information could be found which presented a contrasting position to the position in this petition that attapulgite should be included on the National List as allowed.

References

Patterson, H.B.W. (1992) *Bleaching and Purifying Fats and Oils: Theory and Practice*, AOCS Press, Champaign, Illinois, 242 pages.

Brooks, David D. (1999) Bleaching factors that effect oil loss, *Proceedings of 1999 Palm Oil Research Institute of Malaysia Congress: Emerging Technologies and Opportunities in the Next Millennium*, 45-51.

Brooks, David D. (2000) Bleaching considerations for "organic" oils, presented at the World Conference and Exhibition on Oilseed Processing and Utilization, November 2000.

Zschau, Werner, Bleaching (2000), Chapter 9, p. 159, *Introduction to Fats and Oils Technology*, Second Edition, AOCS Press, Champaign, Illinois.

Exhibit 2

References continued

Yoo, Cheah Kien and Siew Wai Lin (1999) Relationship between Physical Properties of Bleaching Earths and its Bleaching Efficiency on Palm Oil, *Proceedings of 1999 Palm Oil Research Institute of Malaysia Congress: Emerging Technologies and Opportunities in the Next Millennium*, 36-44.

Exhibit 3

Research Information regarding Attapulgite as an Animal Feed Additive

Spent bleaching clay which is removed from filter presses at the back end of the bleaching clay process for animal an vegetable oils is generally disposed of in two ways: 1) It is placed in landfills; 2) It is blended into animal feeds to provide additional nutrition from the absorbed oil on the clay filter cake.

Werner Zschau (Exhibit 22) mentions a reference (Schwarting 1993) in which tests with pigs, poultry, and cattle showed that 3% spent bleaching earth may be added to the feed without any problems. Neither deficiency in vitamin A nor mineral requirements was observed. An article by Wing-Keonig Ng (Exhibit 23) showed that in fishmeal-based diets for Nile tilapia, palm oil-laden spent bleaching clay can totally replace added fish oil.

No research information could be found which presented a contrasting position to the position in this petition that attapulgite should be included on the National List as allowed.

References

Ng, Wing-Keonig, C.-B. Koh, and Z.B. Din, Palm oil-laden spent bleaching clay as a substitute for marine fish oil in the diets of Nile tilapia, *Oreochromis niloticus*, *Aquaculture Nutrition*, Vol. 12, Issue 6, pages 459-468, November 2, 2006.

Zschau, Werner, Bleaching (2000), Chapter 9, p. 176, *Introduction to Fats and Oils Technology*, Second Edition, AOCS Press, Champaign, Illinois.

Exhibit 4

Petition Justification Statement
for
Inclusion of a Non-Synthetic, Non-Agricultural Substance onto the National List, §205.605(a)

Petition Objective:

This petition requests the inclusion of the mineral attapulgite (Fuller's earth) on the approved National List as a bleaching earth for vegetable and animal oils and as a feed additive (in the form of spent bleaching cake). The petitioner believes that it has all the attributes for inclusion.

- Attapulgite is a naturally-occurring clay-like substance.
- Its processing includes only drying and pulverizing, and includes no chemical treatment. The processing does not change the chemical nature of attapulgite; it only removes water and reduces the particle size.
- In its applications, attapulgite does not change the chemical nature of the material to which it is added except for the removal of undesirable color, metals, odor, and other unwanted substances from vegetable and animal oils.
- Contact of "organic" oil with a natural earth such as attapulgite will not adulterate the natural organic nature of the oil.
- Attapulgite is very similar in character to bentonite which is allowed on the National List.

Explanation for need:

1. Bleaching earth. Attapulgite is used as a natural bleaching earth in the purification of vegetable and animal oils. This mineral via the mechanism of adsorption removes chlorophyll and trace impurities such as metals, peroxides, soaps, tocopherols and carotenes from the oil. The removal of these impurities significantly improves the quality of the oil, both its appearance and its stability. No other natural clays meet the efficacy of this material for this application.

2. Animal feed additive. The spent filter cake from the bleaching process mentioned previously is used as an additive to animal feeds to provide economical, additional nutritional value from the absorbed oil on the attapulgite.

Description of non-synthetic or synthetic substances on the National List or alternative cultural methods that could be used in place of the petitioned substance:

1. Bleaching earth. There are no non-synthetic or synthetic substances on the National List that could be used in place of the petitioned synthetic substance as a natural bleaching earth for vegetable/animal oils. Acid activated clays are used as a bleaching earth for vegetable and animal oils, but they are prohibited from use in bleaching organic oils.

Exhibit 4

2. Animal feed additive. No clay substances on the National List are used as a nutritional additive to animal feeds. Only the spent filter cake from the oil bleaching process offers this unique, economical opportunity.

Description of beneficial effects on the environment, or human health from the use of the petitioned substance instead of the use of non-synthetic or synthetic substances on the National List or alternative cultural methods.

1. Bleaching earth. There are no substitutes for the petitioned substance on the National List by which to make a comparison of environmental or human health beneficial effects. The natural bleaching clay which is the subject of this petition, however, does offer an important environmental benefit over conventional acid activated bleaching clays in that it does not generate the substantial amount of acidic rinse water contamination associated with the manufacture of acid activated bleaching earth.

2. Animal feed additive. The use of the petitioned substance in the form of filter cake as an animal feed nutritional additive is beneficial to the environment in that it is a low energy form of nutritional additive. There are no other substances on the List that offer this advantage.

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Exhibit 5

DEPARTMENT OF HEALTH & HUMAN SERVICES

Public Health Service

Food and Drug Administration
Washington DC 20204

July 9, 1993

Ms. Heidi M. Jaffee
Oil-Dri Corporation of America
520 North Michigan Avenue
Chicago, IL 60611

Dear Ms. Jaffee:

This is in reference to your letter of March 30, 1993, requesting our opinion concerning the use of a surface modified, acid activated mineral (Fuller's Earth) adsorbent for decolorizing oils with high chlorophyll levels and hard to bleach colored oils. The material is composed primarily of silicon dioxide (68.54% by weight), aluminum oxide (14%), magnesium oxide (6%), and ferric oxide (5.4%), with smaller amounts of calcium oxide, titanium oxide, and manganese oxide. It is added to heated edible oil, held as a slurry with agitation for a given time period, and is subsequently removed by filtration.

We have completed our review of your request and conclude that because the inorganic matrix of your activated mineral adsorbent is expected to be relatively inert and highly insoluble in the edible oil, there is little or no likelihood of significant amounts of the adsorbent remaining in the oil after filtration. Therefore, the intended use of the subject acid activated Fuller's Earth does not require an amendment to the food additive regulations.

Sincerely yours,

/for

Eugene C. Coleman
Director
Division of Petition Control
Center for Food Safety
and Applied Nutrition

Exhibit 6

THE ISLAMIC FOOD AND NUTRITION COUNCIL OF AMERICA
ألمجلس ألأسلامي ألأمريكي للغذاء و التغذية

IFANCA HALAL PRODUCT CERTIFICATE

Certificate No.: **ODC. 08006**

September 4, 2008

OIL-DRI CORPORATION OF AMERICA
410 N. Michigan Avenue Suite 400
Chicago, IL 60611 USA

To Whom It May Concern:

This is to certify that the following product(s) manufactured and marketed by the **OIL DRI CORPORATION OF AMERICA,** at Ochlocknee, Georgia plant are **Halal** for use into the **Halal** products.

The Company may use the **Crescent M Halal** logo, the IFANCA'S HALAL CERTIFICATION SYMBOL.

1. **Pure-Flo® B80 Natural**
2. **Pure-Flo® B80 CG**
3. **Pure-Flo® M85/20**
4. **Pure-Flo® Supreme B81**
5. **Pure-Flo® Supreme Pro-Active**
6. **Pure-Flo® Supreme Color Master**
7. **Pure-Flo® Perform 6000**
8. **Perform™ 4000**
9. **Perform™ 5000**
10. **Perform™ 5000 CG**
11. **Select™ 350**
12. **Select™ 450**

This certificate is valid until **September 30, 2009,** and subject to renewal at that time.

Muhammad Munir Chaudry
Muhammad Munir Chaudry, Ph.D.
Halal Administrator

SEAL

1982

IFANCA Halal Research Center • 777 Busse Highway • Park Ridge, Illinois 60068 USA • Tel: 847-993-0034 • Fax: 847-993-0038

WWW.IFANCA.ORG

Exhibit 7

בס״ד

Orthodox Union
Letter of Certification

Union of Orthodox Jewish Congregations of America
איחוד קהילות האורתודוקסים באמריקה

December 01, 2008

Oil-Dri Corporation of America (continued)

This is to certify that the following product(s) prepared by this company are under the supervision of the Kashruth Division of the Orthodox Union and are kosher as indicated below.

Product Name	UKD-ID	Status	Certification Requirements
Brand: Pure-Flo (continued)			
• B80	OUW3-08CEB3C	Pareve	Ⓤ Symbol required. Certified for Passover and year-round use.
• B80 CG	OUW3-0CDA13C	Pareve	Ⓤ Symbol required. Certified for Passover and year-round use.
• B81	OUW3-353B70E	Pareve	Ⓤ Symbol required. Certified for Passover and year-round use.
• Color Master	OUW3-9440835	Pareve	Ⓤ Symbol required. Certified for Passover and year-round use.
• L07509	OUV3-EFE33CC	Pareve	Ⓤ Symbol required.
• M-85/20	OUW3-B02808E	Pareve	Ⓤ Symbol required. Certified for Passover and year-round use.

Placing the OU logo on products not listed above constitutes an unauthorized use of the OU symbol, which is a federally registered trademark.

Menachem Genack

Rabbi Menachem Genack, *Rabbinic Administrator, CEO*

This certification is valid through 11/30/2009

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Exhibit 8

The Symbol Scheme
Soil Association
Organic Marketing Company Ltd

SOIL ASSOCIATION ORGANIC STANDARD
Organic Farming EEC Control System
UKROFS registered no. 01051194

Mr I Rawlins
Oil Dry UK Ltd
Bannister Row
Wisbech
Cambridgeshire
PE13 3HZ

To: Dr. Bob Ross

2p.

7th April 1997

Dear Ian,

Pure Flo B80

We are pleased to confirm that your product **Pure Flow B80**, being a form of bentonite, may be used as a processing aid in organic food processing.

A copy of section 8.5 of the current issue of our Standards for Organic Food and Farming is enclosed. This gives the full list of permitted processing aids.

Please let us know if we can be of any further assistance.

Yours sincerely,

Bill Starling

Bill Starling
(Inspector)

86 Colston Street, Bristol BS1 5BB. tel. 0117 - 929 0661 fax: 0117 - 925 2504
Company Registration no 726903 A wholly owned subsidiary of the Soil Association. reg charity no 206862

8.5 PERMITTED PROCESSING AIDS AND OTHER PRODUCTS

8.501 Processing Aids

Name	*Specific Conditions*
Water	-
Calcium chloride	*Coagulation agent*
Calcium carbonate	-
Calcium hydroxide	(Prohibited from 1/1/97)
Calcium sulphate	*Coagulation agent*
Magnesium chloride (or nigari)	*Coagulation agent*
Potassium carbonate	*Drying of grapes*
Carbon dioxide	-
Nitrogen	-
Ethanol	*Solvent*
Tannic acid	*Filtration aid*
Egg white albumen	-
Casein	-
Gelatin	-
Isinglass	-
Vegetable oils	*Greasing or releasing or anti-foaming agent*
Silicon dioxide gel or colloidal solution	-
Activated carbon	-
Talc	(Prohibited from 1/1/97)
Bentonite	-
Kaolin	(Prohibited from 1/1/97)
Diatomaceous earth	-
Perlite	-
Hazelnut shells	-
Beeswax	*Releasing agent*
Carnauba wax	*Releasing agent*
Sodium carbonate	*Sugar production*
Sodium hydroxide	*Sugar production, olive treatment*
Sulphuric acid	*Sugar production*
Rice meal	-

8.502 Preparations of Micro-organisms and Enzymes

1) *Any preparations of micro-organisms and enzymes normally used as processing aids in food processing, with the exception of micro-organisms or preparations of micro-organisms genetically modified in the meaning of Article 2(2) of Directive 90/220/EEC. Article 2(2) of Directive 90/220/EEC is given in paragraph 8.308.*

MAY - 1 2009

Exhibit 9

I

(Acts whose publication is obligatory)

COMMISSION DIRECTIVE 2001/30/EC

of 2 May 2001

amending Directive 96/77/EC laying down specific purity criteria on food additives other than colours and sweeteners

(Text with EEA relevance)

THE COMMISSION OF THE EUROPEAN COMMUNITIES,

Having regard to the Treaty establishing the European Community,

Having regard to Council Directive 89/107/EEC of 21 December 1988 on the approximation of the laws of the Member States concerning food additives authorised for use in foodstuffs intended for human consumption (1), as amended by Directive 94/34/EC of the European Parliament and of the Council (2) and in particular Article 3(3)(a) thereof,

After consulting Scientific Committee on Food,

Whereas:

(1) It is necessary to establish purity criteria for all additives other than colours and sweeteners mentioned in Directive 95/2/EC of the European Parliament and of the Council of 20 February 1995 on food additives other than colours and sweeteners (3), as last amended by Directive 2001/5/EC (4).

(2) Commission Directive 96/77/EC of 2 December 1996 laying down specific purity criteria on food additives other than colours and sweeteners (5), as last amended by Directive 2000/63/EC (6) set out purity criteria for a number of food additives. This Directive should now be completed with purity criteria for the remaining food additives mentioned in Directive 95/2/EC.

(3) It is necessary to take into account the specifications and analytical techniques for additives as set out in the *Codex Alimentarius* as drafted by the Joint FAO/WHO Expert Committee on Food Additives (JECFA).

(4) The measures provided for in this Directive are in accordance with the opinion of the Standing Committee for Foodstuffs,

HAS ADOPTED THIS DIRECTIVE:

Article 1

Directive 96/77/EC is hereby amended as follows:

In the Annex, the text of the Annex to this Directive shall be added.

Article 2

1. Member States shall bring into force the laws, regulations and administrative provisions necessary to comply with this Directive by 1 June 2002 at the latest. They shall forthwith inform the Commission thereof.

2. When Member States adopt those provisions, they shall contain a reference to this Directive or be accompanied by such a reference on the occasion of their official publication. Member States shall determine how such reference is to be made.

3. Products put on the market or labelled before 1 June 2002 which do not comply with this Directive may be marketed until stocks are exhausted.

Article 3

This Directive shall enter into force on the twentieth day following that of its publication in the *Official Journal of the European Communities.*

Article 4

This Directive is addressed to the Member States.

Done at Brussels, 2 May 2001.

For the Commission

David BYRNE

Member of the Commission

---

(1) OJ L 40, 11.2.1989, p. 27.

(2) OJ L 237, 10.9.1994, p. 1.

(3) OJ L 61, 18.3.1995, p. 1.

(4) OJ L 55, 24.2.2001, p. 59.

(5) OJ L 339, 30.12.1996, p. 1.

(6) OJ L 227, 30.10.2000, p. 1.

Barium	Not more than 25 mg/kg
Chromium	Not more than 100 mg/kg
Copper	Not more than 25 mg/kg
Nickel	Not more than 50 mg/kg
Arsenic	Not more than 3 mg/kg
Mercury	Not more than 1 mg/kg
Cadmium	Not more than 2 mg/kg
Lead	Not more than 10 mg/kg

E 556 CALCIUM ALUMINIUM SILICATE

Synonyms	Calcium aluminosilicate, calcium silicoaluminate, aluminium calcium silicate
Definition	
Chemical name	Calcium aluminium silicate
Assay	Content on the anhydrous basis: — as SiO_2 not less than 44,0 % and not more than 50,0 % — as Al_2O_3 not less than 3,0 % and not more than 5,0 % — as CaO not less than 32,0 % and not more than 38,0 %
Description	Fine white, free-flowing powder
Identification	
A. Positive tests for calcium, for aluminium and for silicate	
Purity	
Loss on drying	Not more than 10,0 % (105 °C, 2h)
Loss on ignition	Not less than 14,0 % and not more than 18,0 on the anhydrous basis (1 000 °C, constant weight)
Fluoride	Not more than 50 mg/kg
Arsenic	Not more than 3 mg/kg
Lead	Not more than 10 mg/kg
Mercury	Not more than 1 mg/kg

E 558 BENTONITE

Definition	Bentonite is a natural clay containing a high proportion of montmorillonite, a native hydrated aluminium silicate in which some aluminium and silicon atoms were naturally replaced by other atoms such as magnesium and iron. Calcium and sodium ions are trapped between the mineral layers. There are four common types of bentonite: natural sodium bentonite, natural calcium bentonite, sodium-activated bentonite and acid-activated bentonite

Exhibit 10

2008 Official Publication Association of American Feed Control Officials Incorporated

http://www.aafco.org

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Foreign orders, $65.00 per copy

ISBN 1-878341-20-0

By Association of American Feed Control Officials

87.5 Additional Special Purpose Products:

Name	FDA Regulation	Classification Under Food Additives Amendment	Limitations or Restrictions
Aloe Vera Gel Concentrate		Flavoring agent	Not to exceed 125 ppm (0.0125%) in finished feed
Aluminum Sulfate IFN 8-20-861	Reg. 582.1125	Anti-gelling agent for molasses, dewater of beet pulp	**None
Anise Seed IFN 8-00-416	Reg. 582.10	Spices seasonings, essential oils, oleo resins, and natural extractives	**None
Astaxanthin	21 CFR 73.35	Tissue pigmentor	Salmonid feed only
Attapulgite Clay IFN 8-14-008	Reg. 582.1 (in non-medicated feeds)	Anti-caking agent and pelleting aid Suspension aid in liquid feed supplement	***Not to exceed 2% in finished feed ***Not to exceed 2.5% in supplement
Ball Clay			Not accepted for use as a feed ingredient
Calcium Silicate IFN 8-08-043	Reg. 573.260	Anti-caking agent	Not to exceed 2%
Calcium Aluminates		Pellet binder	Maximum of 2% in poultry, swine and rodent feeds, and a maximum 1% in feed for all other species.
Calcium Stearate IFN 8-09-345	Reg. 573.280 (Feed Grade)	Anti-caking agent	In accordance with good manufacturing practice
Canthaxanthin	21 CFR 73.75	Broiler chicken skin pigmentor	Not to exceed 4 grams/ ton of the complete feed
Carrageenan	21 CFR 172.620	Emulsifier, stabilizer or thickener for pet foods.	To be refined only from those red seaweed sources listed in 21CFR 172.620
Capsicum; Red Pepper IFN 8-03-685	Reg. 582.10	Spices, seasonings, etc.	**None
Chondrus extract IFN 8-07-247	Reg. 582.7255	Stabilizer	None
Diacetyl tartaric acid esters of mono and diglycerides of edible fats or oils, or edible fat-forming fatty acids. IFN 8-07-248	Reg. 582.4101	Emulsifying Agent	None
Diatomaceous Earth IFN 8-09-363	Reg. 573.340	Inert Carrier and Anti-caking agent	Not to exceed 2% of total ration
Disodium EDTA IFN 8-05-689	Reg. 573.360	To solubilize trace minerals in aqueous solutions.	Not to exceed 0.024% (240 ppm) in finished feed
Ethyl Cellulose IFN 4-08-045	Reg. 573.420	Binder or filler in dry vitamin preparations	
Ethoxylated mono and diglycerides	Reg. 172.834	Emulsifier	Not to exceed 0.5% in dry milk replacers
Fennel IFN 8-01-855	Reg. 582.10	Spices, seasonings, essential oils, etc.	**None
Fenugreek Seed IFN 8-01-856	Reg. 582.10	Spices, seasonings, essential oils, etc.	**None
Fumaric Acid		pH adjuster, preservative, or flavoring agent	Not to exceed 0.5% of the diet
Gellan Gum	21 CFR 172.665	Stabilizer and/or	Not to exceed 0.4% in

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Exhibit 11

EUROPEAN COMMISSION

TöGEthé®
SINCE 1957

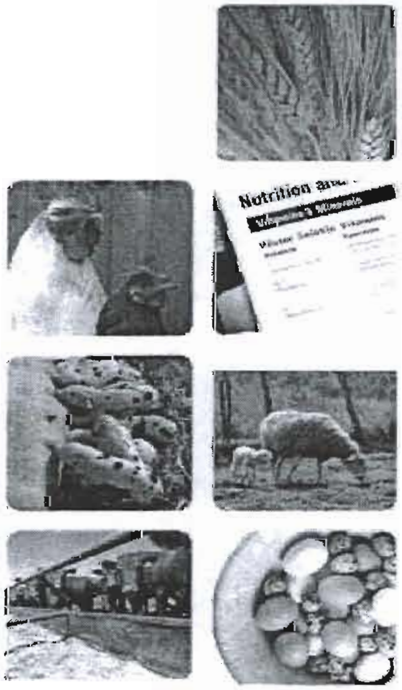
Health & Consumer Protection
Directorate-General

Community Register of Feed Additives
pursuant to Regulation (EC) No 1831/2003

Appendixes 3 & 4.
Annex : List of additives

(Status: Released 23 April 2009.)
[Rev. 48]

Directorate D - Animal Health and Welfare
Unit D2 - Feed



- Correction of 6 CAS numbers of products already included.

Additions:

- Reg. (EC) No 479/2006 28.3.2006 L 86/4
- Reg. (EC) No 492/2006 28.3.2006 L 89/6
- Category "chemically defined flavourings" 194 new entries
- Category "natural produtcs botaniclly defined" 31 new entries
- Category "natural products of non plant origin" 2 new entries

2nd edition: published on 16 December 2005

Additions:

- Reg. (EC) No 2036/2005. O.J. L 328 of 15.12.2005 p. 13.
- Category "micro-organisms": changes in entries E 1703, E 1712; new entry E 1713.
- Category "enzymes", new entries E 1636, E 1637, 5, 59; change in entry Enzyme 37.
- Reg. (EC) No 1980/2005 of 05.12.2005 OJ L 318 of 05.12.2005. p. 3 Category Trace elements: E 6 Zinc.
- Reg. (EC) No 2037/2005. O.J. L 328 of 14.12.2005, p21. Category " Coccidiostats and other medicinal substances ", changes in entry E 763 Lasalocid A sodium (Avatec).

Removal:

- Category Antibiotics. The period of authorisation ended 31.12.2005.

1st edition: published on 7 November 2005

Appendix 4: Further information

This Register is available at:
http://ec.europa.eu/food/food/animalnutrition/feedadditives/registeradditives_en.htm

Further information on the Community legislation on feed additives can be found in:
http://ec.europa.eu/food/food/animalnutrition/feedadditives/legisl_en.htm

Category	Functional Group		Code	Additive	Reference(s) of Community legal act		Date of authorisation	Expiry date of authorisation(s)	Date of first entry in the Register
(Annex I of Reg. 1831/03)	*(Annex I of Reg. 1831/03)*	Subclassification			(Title and/or No. of legal measure)	Reference in OJ			
1		Binders, anti-caking agents and coagulants	E 554	Sodium aluminosilicate, synthetic	Council Directive 70/524/EEC concerning additives in feedingstuffs - List of authorised additives in feedingstuffs (2004/C 50/01)	OJ C 50, 25.2.2004, p. 1	-	Subject to the provisions of Art. 10 § 2 of Reg. 1831/2003	07.11.05
1		Binders, anti-caking agents and coagulants	E 558	Bentonite-montmorillonite	Council Directive 70/524/EEC concerning additives in feedingstuffs - List of authorised additives in feedingstuffs (2004/C 50/01)	OJ C 50, 25.2.2004, p. 1	-	Subject to the provisions of Art. 10 § 2 of Reg. 1831/2003	07.11.05
1		Binders, anti-caking agents and coagulants	E 559	Kaolinitic clays, free of asbestos	Council Directive 70/524/EEC concerning additives in feedingstuffs - List of authorised additives in feedingstuffs (2004/C 50/01)	OJ C 50, 25.2.2004, p. 1	-	Subject to the provisions of Art. 10 § 2 of Reg. 1831/2003	07.11.05
1		Binders, anti-caking agents and coagulants	E 560	Natural mixtures of steatites and chlorite	Council Directive 70/524/EEC concerning additives in feedingstuffs - List of authorised additives in feedingstuffs (2004/C 50/01)	OJ C 50, 25.2.2004, p. 1	-	Subject to the provisions of Art. 10 § 2 of Reg. 1831/2003	07.11.05
1		Binders, anti-caking agents and coagulants	E 561	Vermiculite	Council Directive 70/524/EEC concerning additives in feedingstuffs - List of authorised additives in feedingstuffs (2004/C 50/01)	OJ C 50, 25.2.2004, p. 1	-	Subject to the provisions of Art. 10 § 2 of Reg. 1831/2003	07.11.05
1		Binders, anti-caking agents and coagulants	E 562	Sepiolite	Council Directive 70/524/EEC concerning additives in feedingstuffs - List of authorised additives in feedingstuffs (2004/C 50/01)	OJ C 50, 25.2.2004, p. 1	-	Subject to the provisions of Art. 10 § 2 of Reg. 1831/2003	07.11.05
1		Binders, anti-caking agents and coagulants	E 563	Sepiolitic clay	Council Directive 70/524/EEC concerning additives in feedingstuffs - List of authorised additives in feedingstuffs (2004/C 50/01)	OJ C 50, 25.2.2004, p. 1	-	Subject to the provisions of Art. 10 § 2 of Reg. 1831/2003	07.11.05
1		Binders, anti-caking agents and coagulants	E 565	Lignosulphonates	Council Directive 70/524/EEC concerning additives in feedingstuffs - List of authorised additives in feedingstuffs (2004/C 50/01)	OJ C 50, 25.2.2004, p. 1	-	Subject to the provisions of Art. 10 § 2 of Reg. 1831/2003	07.11.05
1		Binders, anti-caking agents and coagulants	E 566	Natrolite-phonolite	Council Directive 70/524/EEC concerning additives in feedingstuffs - List of authorised additives in feedingstuffs (2004/C 50/01)	OJ C 50, 25.2.2004, p. 1	-	Subject to the provisions of Art. 10 § 2 of Reg. 1831/2003	07.11.05
1		Binders, anti-caking agents and coagulants	E 567	Clinoptilolite of volcanic origin (Pigs, Rabbit; Poultry)	Reg. (EC) No 2148/2004 / *Amended by* Reg. (EC) NO 1980/2005 of 05.12.2005	OJ L 370, 17.12.2004, p. 24 / *Amended by* OJ L 318, 05.12.2005, p. 3	-	Subject to the provisions of Art. 10 § 2 of Reg. 1831/2003	16.12.05

Category	Functional Group		Code	Additive	Reference(s) of Community legal act		Date of authorisation	Expiry date of authorisation(s)	Date of first entry in the Register
(Annex I of Reg. 1831/03)	*(Annex I of Reg. 1831/03)*	Subclassification			(Title and/or No. of legal measure)	Reference in OJ			
1	k	3- Substances		Sodium sulphite	Reg. (EC) 1831/2003	OJ L 268, 18.10.2003, p. 29	07.11.2005	Subject to the provisions of Art. 10 § 2 of Reg. 1831/2003	07.11.05
1	k	3- Substances		Sodium thiosulphate	Reg. (EC) 1831/2003	OJ L 268, 18.10.2003, p. 29	07.11.2005	Subject to the provisions of Art. 10 § 2 of Reg. 1831/2003	07.11.05
1	k	3- Substances	E 513	Sulphuric acid	Council Directive 70/524/EEC concerning additives in feedingstuffs - List of authorised additives in feedingstuffs (2004/C 50/01)	OJ C 50, 25.2.2004, p. 1	-	Subject to the provisions of Art. 10 § 2 of Reg. 1831/2003	07.11.05
1	k	3- Substances	E 450 a (iii)	Tetrasodium diphosphate	Reg. (EC) 1831/2003	OJ L 268, 18.10.2003, p. 29	07.11.2005	Subject to the provisions of Art. 10 § 2 of Reg. 1831/2003	07.11.05
1	k	3- Substances		Attapulgite (clay) CAS No. 12174-11-7	Reg. (EC) 1831/2003	OJ L 268, 18.10.2003, p. 29	07.11.2005	Subject to the provisions of Art. 10 § 2 of Reg. 1831/2003	07.11.05
1	k	3- Substances		Tannin extract from sweet chestnut wood (Castanea Sativa Mill, CAS No.1401-55-4)	Reg. (EC) 1831/2003	OJ L 268, 18.10.2003, p. 29	07.11.2005	Subject to the provisions of Art. 10 § 2 of Reg. 1831/2003	07.11.05
2	a	Carotenoids and xanthophylls	E 160c	Capsanthin	Council Directive 70/524/EEC concerning additives in feedingstuffs - List of authorised additives in feedingstuffs (2004/C 50/01)	OJ C 50, 25.2.2004, p. 1	-	Subject to the provisions of Art. 10 § 2 of Reg. (EC) No 1831/2003	07.11.05
2	a	Carotenoids and xanthophylls	E 160e	Beta-apo-8'-carotenal	Council Directive 70/524/EEC concerning additives in feedingstuffs - List of authorised additives in feedingstuffs (2004/C 50/01)	OJ C 50, 25.2.2004, p. 1	-	Subject to the provisions of Art. 10 § 2 of Reg. (EC) No 1831/2003	07.11.05
2	a	Carotenoids and xanthophylls	E 160f	Ethyl ester of beta-apo-8'-carotenoic acid	Council Directive 70/524/EEC concerning additives in feedingstuffs - List of authorised additives in feedingstuffs (2004/C 50/01)	OJ C 50, 25.2.2004, p. 1	-	Subject to the provisions of Art. 10 § 2 of Reg. (EC) No 1831/2003	07.11.05
2	a	Carotenoids and xanthophylls	E 161b	Lutein	Council Directive 70/524/EEC concerning additives in feedingstuffs - List of authorised additives in feedingstuffs (2004/C 50/01)	OJ C 50, 25.2.2004, p. 1	-	Subject to the provisions of Art. 10 § 2 of Reg. (EC) No 1831/2003	07.11.05
2	a	Carotenoids and xanthophylls	E 161c	Cryptoxanthin	Council Directive 70/524/EEC concerning additives in feedingstuffs - List of authorised additives in feedingstuffs (2004/C 50/01)	OJ C 50, 25.2.2004, p. 1	-	Subject to the provisions of Art. 10 § 2 of Reg. (EC) No 1831/2003	07.11.05

Exhibit 12

MAY - 1 2009

Canadian Food Inspection Agency
Agence canadienne d'inspection des aliments

Feeds Regulations, 1983

SCHEDULE IV

Version française

PART I

CLASS 1. DRY FORAGES AND ROUGHAGES

1.1

Alfalfa-grass hay sun-cured ground (or Alfalfa-grass meal) (IFN 1-29-774)
consists of the aerial part of a mixture of alfalfa and grass plants (predominantly alfalfa) that has been sun-cured and finely ground. It shall be labelled with guarantees for minimum crude protein, maximum crude fibre, maximum moisture, minimum alfalfa and minimum grass.

1.2

Alfalfa hay sun-cured ground (or Sun-cured alfalfa meal) (IFN 1-00-111)
consists of the aerial part of the alfalfa plant, reasonably free of other crop plants, weeds and mold, that has been sun-cured and finely ground. It shall be labelled with guarantees for minimum crude protein, maximum crude fibre and maximum moisture.

1.3

Alfalfa leaves meal dehydrated (or Alfalfa leaf meal) (IFN 1-00-137)
consists of leaves of alfalfa separated from the alfalfa plant that have been dried by thermal means and finely ground. It shall be reasonably free of other crop plants and weeds. It shall be labelled with guarantees for minimum crude protein, maximum crude fibre and maximum moisture.

1.4

Alfalfa meal dehydrated (IFN 1-00-025)
consists of the aerial part of the alfalfa plant, reasonably free of other crop plants,weeds and mold, that has been finely ground and dried by thermal means. It shall be labelled with guarantees for minimum crude protein, maximum crude fibre and maximum moisture.

1.5

Alfalfa stems sun-cured ground (or Alfalfa stem meal) (IFN 1-00-165)
consists of the finely ground sun-cured aerial part of the alfalfa plant from which the leaves have been removed. It shall be reasonably free of other crop plants and weeds. It shall be labelled with guarantees for minimum crude protein, maximum crude fibre and maximum moisture.

1.6

Grass-alfalfa hay sun-cured ground (or Grass-alfalfa meal) (IFN 1-29-775)
consists of the aerial part of a mixture of grass and alfalfa plants (predominantly grass) that has been sun-cured and finely ground. It shall be labelled with guarantees for minimum crude protein, maximum crude fibre, maximum moisture, minimum alfalfa and minimum grass.

1.7

Cellulose powdered (or Cellulose) (IFN 1-15-514)
is the purified, mechanically disintegrated polysaccharide consisting of glucose in a beta (1-4) linkage prepared by processing alpha cellulose obtained as a pulp from fibrous plant materials.

1.8

Cereals grass meal dehydrated (or Dehydrated cereal grass) (IFN 1-16-289)
consists of the aerial part of a cereal grass, reasonably free of other crop plants, weeds and mold, that has been finely ground and dried by thermal means. It shall be labelled with guarantees for minimum crude protein, maximum crude fibre and maximum moisture.

1.9

Maize cobs, dehydrated, fine ground (or Corn cobs, dehydrated, fine ground or Fine grind maize cob meal or Fine grind corn cob meal (IFN 1-02-781)
consists of the entire corn cob that has been finely ground and dried by thermal means. It shall be labelled with guarantees for minimum crude protein, maximum crude fibre and maximum moisture.

1.10

Maize, cob fractions, screened (or Corn, cob fractions, screened or Maize cob fractions or Corn cob fractions) (IFN 1-02-779)
consists of the hard woody, ring or beeswing fractions obtained by screening ground corn cobs. It shall be labelled with guarantees for minimum crude protein, maximum crude fibre and maximum moisture.

8.112

Ultramarine blue (IFN - -)
is obtained by calcining a mixture of Kaolin, sulfur, sodium carbonate and carbon at temperatures above 700°C to form a complex sodium aluminum sulfosilicate ($Na_7Al_6Si_6O_2S_3$). It shall be labelled with one or both of the following statements:

"Ultramarine blue is for use as a colouring agent in salt blocks in an amount not to exceed 0.5 per cent by weight of the salt"; or

«Le bleu d'outremer doit être utilisé comme agent colorant dans les blocs de sel en quantité ne dépasser pas 0,5 pour cent du poids du sel.»

8.113

Vermiculite(Granules) (or Verxite (granules)) (IFN 8-18-981)
is a magnesium-iron-aluminum silicate containing a minimum of 98 per cent hydrobiotite. It shall be labelled with one or both of the following statements:

"This product is for use in an amount not to exceed 5.0 per cent of the finished feed"; or

«Ce produit est utilisé en quantité ne devant pas dépasser 5,0 pour cent de l'aliment fini.»

8.114

Wood charcoal (IFN 8-30-460)
is the ground, black, amorphous carbon solid obtained by processing of the wood and is a colouring agent.

8.115

Aluminum hydroxide, (AlH_3O_3) (or Hydrated alumina, or Aluminum hydrate) (IFN - -)
is the hydrated oxide salt of aluminum. It shall be labelled with a guarantee for minimum aluminum hydroxide.

8.116

Annatto seeds, extract (or Annatto extract or Bixa orellana seed extract) (IFN - -)
is the extract of the annatto seed, Bixa orellana which contains bixin and several yellow to orange-red pigments which give carotene reactions, and is a colouring agent.

8.117

Citric ester of mono and di- glycerides (IFN 8 - -)
consists of mixture of Mono and Di- glycerides in a citric ester matrix.

8.118

Attapulgite clay (IFN 8-14-008)
is hydrated aluminum - magnesium silicae, a naturally occurring mineral mined in Attapulgus, Georgia. The chemical formula is ($(Mg, Al)_5Si_8O_{22}(OH)_4.4H_2O$. It shall be labelled with the following statement:

"This product is for use in non-medicated feeds only as an anticaking agent or pelleting aid in an amount not to exceed 0.25% of the finished feed or as an emulsifier in liquid feed supplements at a level not to exceed 2.5% of the supplement."

«Ce produit est ajouté aux aliments du bétail non médicamenteux seulement comme anti-agglomérant ou comme agent de pellétisation, en quantité ne dépassant pas 0,25 % de l'aliment fini, ou comme émulsifiant dans les suppléments liquides d'aliments du bétail, cans une proportion maximale de 2,5% du supplément.»

8.119

D-Mannitol (or Mannitol,D-) (IFN - - -)
is the product of a reduction process by either H_2 gas in the presence of metal catalysts (platinum) or sodium amalgam in water with mannose.

8.120

Sorbitan monostearate (IFN - - -)
is a mixture of stearic and palmidic acid esters of sorbitol and their mono- and di-anhydrides.

8.121

Gelatin (IFN - - -)
is the product obtained by partial hydrolysis of collagen derived from animal skin, white connective tissue and bones. If the product is or may consist of ruminant material, other than skin and hides, it shall be labelled with the following statement(s) required by the Minister, in English and/or French: "Feeding this product to cattle, sheep, deer or other ruminants is illegal and Is subject to fines or other punishments under the Health of Animals Act" and/or « Il est interdit d'en nourrir les boeufs, moutons, cerfs et autres ruminants et des amendes ou autres peines sont prévues à égard par la Loi sur la santé des animaux. »

8.122

Triethyl citrate (or Triethyl citrate (ethyl citrate)) (IFN - - -)
is an emulsifier

8.123

Allura Red Dye (or Red Dye #40, or FD&C Red #40, or FD&C #40) (IFN ----)
is a 6-hydroxy-5-[(2-methoxy-5-methyl-4-sulphophenyl)azo]-2-naphthalene sulfonic acid disodium salt and is used as a colouring agent. This dye is not to be used at levels exceeding 30 ppm in lactating dairy feeds.

8.124

Feeds Regulations, 1983

SCHEDULE IV - PART I

INDEX

* *International Feed Name*

** *International Feed Number*

CLASS 8. MISCELLANEOUS PRODUCTS

8.1

Acetic acid (IFN 8-19-655)
is ethanoic acid.

8.2

Animal bone collagen hydrolysed (IFN 8-16-472)
is the dried ground collagen colloid obtained after removal of the fat and minerals from the hydrolysis of clean undecomposed ground beef bone under heat and pressure. It shall be labelled with one or both of the following statements:

"This product is for use in feeds as a pelleting aid. Consult the Compendium of Medicating Ingredient Brochures for acceptable drug compatibilities with this product"; or

«Ce produit est destiné à être utilisé comme agent de pelletisation dans les aliments du bétail. Consulter le Recueil des notices sur les substances médicatrices pour connaître les compatibilités de médicaments acceptables avec ce produit.»

If the product contains "prohibited material" as set forth in Section 162(1) of the *Health of Animals Regulations*, it shall be labelled with the following statement(s) required by the Minister, in English and/or French: "Feeding this product to cattle, sheep, deer or other ruminants is illegal and is subject to fines or other punishments under the Health of Animals Act" and/or « Il est interdit d'en nourrir les boeufs, moutons, cerfs et autres ruminants et des amendes ou autres peines sont prévues à égard par la Loi sur la santé des animaux. »

8.3

Ascorbyl palmitate (IFN 8-26-245)
is 6-hexadecanoate L-ascorbic acid.

8.4

Barley malt flour dehydrated (or Dried barley malt flour or Malted barley flour of Malt diastase) (IFN8-16-303)
is obtained by milling cleaned malted barley for the production of diastase. It shall be labelled with guarantees for minimum amylase enzyme activity.

8.5

Bentonite calcium (IFN 8-00-695)
is a naturally occurring mineral consisting primarily of montmorillonite (a tri-layered aluminum silicate). It contains calcium as the predominant available or exchange ion. It shall be labelled with one or both of the following statements:

"This product is for use in feeds as an anticaking agent or pelleting aid in an amount not to exceed 2 percent of the total diet. Consult the Compendium of Medicating Ingredient Brochures for acceptable drug compatibilities with this product."; or

«Ce produit est destiné à être utilisé comme agent antiagglutinant ou de pelletisation dans les aliments du bétail, en quantité ne devant pas dépasser 2 pour cent de la ration totale. Consulter le Recueil des notices sur les substances médicatrices pour connaître les compatibilités de médicaments acceptables avec ce produit.»

It shall also be labelled with guarantees for minimum calcium and maximum moisture.

8.6

Bentonite sodium (IFN 8-14-512)
is a naturally occurring mineral consisting primarily of montmorillonite (a tri-layered aluminum silicate). It contains sodium as the predominant available or exchange ion. It shall be labelled with one or both of the following statements:

"This product is for use in feeds as an anticaking agent or pelleting aid in an amount not to exceed 2 percent of the total diet. Consult the Compendium of Medicating Ingredient Brochures for acceptable drug compatibilities with this product."; or

«Ce produit est destiné à être utilisé comme agent antiagglutinant ou de pelletisation dans les aliments du bétail, en quantité ne devant pas dépasser 2 pour cent de la ration totale. Consulter le Recueil des notices sur les substances médicatrices pour connaître les compatibilités de médicaments acceptables avec ce produit.»

It shall also be labelled with guarantees for minimum sodium and maximum moisture.

8.7

Benzoic acid (IFN 8-26-244)
is benzenecarboxylic acid. It shall be labelled with one or both of the following statements:

"This product is for use as a preservative in an amount not to exceed 0.1 percent."; or

«Ce produit est destiné à être utilisé comme agent de conservation en quantité ne devant pas dépasser 0,1 pour cent.»

8.8

Brilliant Blue FCF lake (or FD & C Blue No. 1 lake)(IFN 8-15-911)
is the disodium salt of N-ethyl-N-(4-((4-(ethyl((3-sulfophenyl)methyl)amino) phenyl)methylene)-2,5-cyclohadien-1-ylidene) -3 -sulfobenzenemethanaminium hydroxide inner salt and is a colouring agent. It shall be labelled with a guarantee for minimum primary dye content.

8.9

Butylated hydroxyanisole (or Butylated hydroxyanisole (BHA)) (IFN 8-01-044)
is 2-5-butyl-4-methoxy phenol. It shall be labelled with one or both of the following statements:

"This product is for use as an antioxidant at a level not to exceed 0.02 percent (butylated hydroxyanisole plus butylated hydroxytoluene) of the fat or oil content of the complete feed"; or

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Exhibit 13

OMRI Products List

A DIRECTORY OF PRODUCTS SUITABLE FOR USE IN CERTIFIED ORGANIC PRODUCTION

2007

Crop

Livestock

Processing and Handling

OMRI®
Listed

CATEGORIES

Processing and Handling Products

Agricultural Ingredients and Processing Aids

Defoamers **A**

FOAM BLAST® ORG 31 (Emerald Performance Materials, LLC)

Non-agricultural Ingredients and Processing Aids

Ascorbic Acid **A**

NatureSeal® AS-5 (Mantrose-Haeuser Co., Inc.)
NatureSeal® PS-10 (Mantrose-Haeuser Co., Inc.)

Bentonite **A**

Redmond Clay (Redmond Trading Company, L.C.)
Veegum® Pure (R. T. Vanderbilt Co, Inc.)

Carbon Dioxide **A**

Tectrol® Atmospheres (TransFRESH Corp.)
Tectrol® Controlled Atmosphere System (TransFRESH Corp.)

Defoamers **A**

FOAM BLAST® ORG 40 (Emerald Performance Materials, LLC)
FOAM BLAST® ORG 50 (Emerald Performance Materials, LLC)
FOAM BLAST® ORG 51 (Emerald Performance Materials, LLC)
Foam Blast® RKD (Emerald Performance Materials, LLC)

Ethylene **R**

CJS Ethylene Filters Bulk Pellets (CJS Ethylene Filters)
CJS Ethylene Filters Sachets (CJS Ethylene Filters)

Glycerin **A**

Glycamed (Glaconchemie)

Packing Material **A**

E.G.G. Ethylene Gas Guardian (Ethylene Control, Inc.)
Ethylene Control Power Pellets (Ethylene Control, Inc.)

Salt **A**

Redmond Real Salt® (Redmond Trading Company, L.C.)

Wax **A**

Decco Citrus Lustr® 520 Organic (Decco Cerexagri, Inc.)
Decco Lustr® 505 Organic (Decco Cerexagri, Inc.)
Natralife BC-Z 646 (Natratec International Ltd.)

Pest Controls

Botanical Pesticides **R**

PyGanic® Crop Protection EC 5.0 II (MGK Co.)
Safer® Brand Ant Killer (Woodstream Corporation)
Victor Poison-Free® Ant & Roach Killer (Woodstream Corporation)

Diatomaceous Earth **R**

Chemfree Insectigone® Ant Killer (Woodstream Corporation)
Chemfree Insectigone® Crawling Insect Killer (Woodstream Corporation)
Concern® Diatomaceous Earth Crawling Insect Killer (Woodstream Corporation)
Insecto An Insecticide For Control of Grain Insects and House Insects (Natural Insecto Products)

D-limonene **R**

Orange Guard® (Orange Guard, Inc.)

Pseudomonas **A**

Bio-Save® 10 LP (JET Harvest Solutions)

Pyrethrum **R**

PyGanic® Pro (MGK Co.)

Processing Sanitizers and Cleaners

Chlorine Materials **R**

Oxine® (Bio-Cide International, Inc.)
The Disinfectant Answer® (Environmental Care and Share)

Detergents **R**

Cafiza™ Espresso Machine Cleaner (Urnex® Brands, Inc.)
Cleancaf® Cleaner & Descaler (Urnex® Brands, Inc.)
EVO Espresso Machine Cleaner (Cafetto)
Puro Caff® Espresso Machine Cleaner (Urnex® Brands, Inc.)
The Cleaner Answer® (Environmental Care and Share)
Triple 7 Colloidal Concentrate (Environmental Fluid Systems)
Triple 7 Envirobore (Environmental Fluid Systems)
Triple 7 Enviroscale Acid (Environmental Fluid Systems)
Triple 7 Heavy Duty (Environmental Fluid Systems)
Triple 7 Odour Control (Environmental Fluid Systems)
Triple 7 Odourex (Environmental Fluid Systems)
Triple 7 Supersolve (Environmental Fluid Systems)
Urnex® Urn & Brewer Cleaner (Urnex® Brands, Inc.)

D-limonene **R**

Orange TKO (Orange TKO Industries International, Inc.)

Peracetic acid **A**

FMC - 323 (FMC Corporation)
Tsunami® 100 (Eco Lab, Inc.)
VigorOx® 15 F&V (FMC Corporation)
VigorOx® Citrus XA (FMC Corporation)
VigorOx® Liquid Sanitizer and Disinfectant (FMC Corporation)
VigorOx® SP-15 Antimicrobial Agent (FMC Corporation)

A: The product is allowed.

R: Use restrictions are required for compliant use under the NOP Rule. This status is assigned when one or more ingredients are Restricted on the OMRI Generic Materials List.

Exhibit 14

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Justia> Law> United States> Code of Federal Regulations> Title 7 - Agriculture> CHAPTER I--AGRICULTURAL MARKETING SERVICE (Standards, Inspections, Marketing Practices), DEPARTMENT OF AGRICULTURE> PART 205--NATIONAL ORGANIC PROGRAM > § 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))."

7 C.F.R. § 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))."

Title 7 - Agriculture

Title 7: Agriculture
PART 205—NATIONAL ORGANIC PROGRAM
Subpart G—Administrative
The National List of Allowed and Prohibited Substances

Browse Previous | Browse Next

§ 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))."

The following nonagricultural substances may be used as ingredients in or on processed products labeled as "organic" or "made with organic (specified ingredients or food group(s))" only in accordance with any restrictions specified in this section.

(a) *Nonsynthetics allowed:*

Acids (Alginic; Citric—produced by microbial fermentation of carbohydrate substances; and Lactic).

Agar-agar.

Animal enzymes—(Rennet—animals derived; Catalase—bovine liver; Animal lipase; Pancreatin; Pepsin; and Trypsin).

Bentonite.

Calcium carbonate.

Calcium chloride.

Calcium sulfate—mined.

Carageenan.

Colors, nonsynthetic sources only.

Dairy cultures.

Diatomaceous earth—food filtering aid only.

Enzymes—must be derived from edible, nontoxic plants, nonpathogenic fungi, or nonpathogenic bacteria.

Flavors, nonsynthetic sources only and must not be produced using synthetic solvents and carrier systems or any artificial preservative.

Glucono delta-lactone—production by the oxidation of D-glucose with bromine water is prohibited.

Kaolin.

Magnesium sulfate, nonsynthetic sources only.

Nitrogen—oil-free grades.

Oxygen—oil-free grades.

Perlite—for use only as a filter aid in food processing.

Potassium chloride.

Potassium iodide.

Sodium bicarbonate.

Sodium carbonate.

Tartaric acid.

Waxes—nonsynthetic (Camauba wax; and Wood resin).

Yeast—nonsynthetic, growth on petrochemical substrate and sulfite waste liquor is prohibited (Autolysate; Bakers; Brewers; Nutritional; and Smoked—nonsynthetic smoke flavoring process must be documented).

(b) *Synthetics allowed:*

Alginates.

Ammonium bicarbonate—for use only as a leavening agent.

Ammonium carbonate—for use only as a leavening agent.

Ascorbic acid.

Calcium citrate.

Calcium hydroxide.

Calcium phosphates (monobasic, dibasic, and tribasic).

Carbon dioxide.

Cellulose—for use in regenerative casings, as an anti-caking agent (non-chlorine bleached) and filtering aid.

Chlorine materials—disinfecting and sanitizing food contact surfaces, *Except,* That, residual chlorine levels in the water shall not exceed the maximum residual disinfectant limit under the Safe Drinking Water Act (Calcium hypochlorite; Chlorine dioxide; and Sodium hypochlorite).

Ethylene—allowed for postharvest ripening of tropical fruit and degreening of citrus.

Ferrous sulfate—for iron enrichment or fortification of foods when required by regulation or recommended (independent organization).

Glycerides (mono and di)—for use only in drum drying of food.

Glycerin—produced by hydrolysis of fats and oils.

Hydrogen peroxide.

Lecithin—bleached.

Magnesium carbonate—for use only in agricultural products labeled “made with organic (specified ingredients or food group(s)),” prohibited in agricultural products labeled “organic”.

Magnesium chloride—derived from sea water.

Magnesium stearate—for use only in agricultural products labeled “made with organic (specified ingredients or food group(s)),” prohibited in agricultural products labeled “organic”.

Nutrient vitamins and minerals, in accordance with 21 CFR 104.20, Nutritional Quality Guidelines For Foods.

Ozone.

Pectin (low-methoxy).

Phosphoric acid—cleaning of food-contact surfaces and equipment only.

Potassium acid tartrate.

Potassium tartrate made from tartaric acid.

Potassium carbonate.

Potassium citrate.

Potassium hydroxide—prohibited for use in lye peeling of fruits and vegetables except when used for peeling peaches during the Individually Quick Frozen (IQF) production process.

Potassium iodide—for use only in agricultural products labeled “made with organic (specified ingredients or food group(s)),” prohibited in agricultural products labeled “organic”.

Potassium phosphate—for use only in agricultural products labeled “made with organic (specific ingredients or food group(s)),” prohibited in agricultural products labeled “organic”.

Silicon dioxide.

Sodium citrate.

Sodium hydroxide—prohibited for use in lye peeling of fruits and vegetables.

Sodium phosphates—for use only in dairy foods.

Sulfur dioxide—for use only in wine labeled “made with organic grapes,” Provided, That, total sulfite concentration does not exceed 100 ppm.

Tartaric acid.

Tocopherols—derived from vegetable oil when rosemary extracts are not a suitable alternative.

Xanthan gum.

(c)–(z) [Reserved]

[68 FR 61993, Oct. 31, 2003, as amended as 68 FR 62217, Nov. 3, 2003]

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Exhibit 15

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☐ **1:** Int J Toxicol. 2003;22 Suppl 1:37-102.

Links

Final report on the safety assessment of aluminum silicate, calcium silicate, magnesium aluminum silicate, magnesium silicate, magnesium trisilicate, sodium magnesium silicate, zirconium silicate, attapulgite, bentonite, Fuller's earth, hectorite, kaolin, lithium magnesium silicate, lithium magnesium sodium silicate, montmorillonite, pyrophyllite, and zeolite.

Elmore AR; Cosmetic Ingredient Review Expert Panel.

This report reviews the safety of Aluminum, Calcium, Lithium Magnesium, Lithium Magnesium Sodium, Magnesium Aluminum, Magnesium, Sodium Magnesium, and Zirconium Silicates, Magnesium Trisilicate, Attapulgite, Bentonite, Fuller's Earth, Hectorite, Kaolin, Montmorillonite, Pyrophyllite, and Zeolite as used in cosmetic formulations. The common aspect of all these claylike ingredients is that they contain silicon, oxygen, and one or more metals. Many silicates occur naturally and are mined; yet others are produced synthetically. Typical cosmetic uses of silicates include abrasive, opacifying agent, viscosity-increasing agent, anticaking agent, emulsion stabilizer, binder, and suspending agent. Clay silicates (silicates containing water in their structure) primarily function as adsorbents, opacifiers, and viscosity-increasing agents. Pyrophyllite is also used as a colorant. The International Agency for Research on Cancer has ruled Attapulgite fibers >5 microm as possibly carcinogenic to humans, but fibers <5 microm were not classified as to their carcinogenicity to humans. Likewise, Clinoptilolite, Phillipsite, Mordenite, Nonfibrous Japanese Zeolite, and synthetic Zeolites were not classified as to their carcinogenicity to humans. These ingredients are not significantly toxic in oral acute or short-term oral or parenteral toxicity studies in animals. Inhalation toxicity, however, is readily demonstrated in animals. Particle size, fibrogenicity, concentration, and mineral composition had the greatest effect on toxicity. Larger particle size and longer and wider fibers cause more adverse effects. Magnesium Aluminum Silicate was a weak primary skin irritant in rabbits and had no cumulative skin irritation in guinea pigs. No gross effects were reported in any of these studies. Sodium Magnesium Silicate had no primary skin irritation in rabbits and had no cumulative skin irritation in guinea pigs. Hectorite was nonirritating to the skin of rabbits in a Draize primary skin irritation study. Magnesium Aluminum Silicate and Sodium Magnesium Silicate caused minimal eye irritation in a Draize eye irritation test. Bentonite caused severe iritis after injection into the anterior chamber of the eyes of rabbits and when injected intralamellarly, widespread corneal infiltrates and retrocorneal membranes were recorded. In a primary eye irritation study in rabbits, Hectorite was moderately irritating without washing and practically nonirritating to the eye with a washout. Rats tolerated a single dose of Zeolite A without any adverse reaction in the eye. Calcium Silicate had no discernible effect on nidation or on maternal or fetal survival in rabbits. Magnesium Aluminum Silicate had neither a teratogenic nor adverse effects on the mouse fetus. Female rats receiving a 20% Kaolin diet exhibited maternal anemia but no significant reduction in birth weight of the pups was recorded. Type A Zeolite produced no adverse effects on the dam, embryo, or fetus in either rats or rabbits at any dose level. Clinoptilolite had no effect on female rat reproductive performance. These ingredients were not genotoxic in the Ames bacterial test system. In primary hepatocyte cultures, the addition of Attapulgite had no significant unscheduled DNA synthesis. Attapulgite did cause significant increases in unscheduled DNA synthesis in rat pleural mesothelial cells, but no significant increase in sister chromosome exchanges were seen. Zeolite particles (<10 microm) produced statistically significant increase in the percentage of aberrant metaphases in human peripheral blood lymphocytes and cells collected by peritoneal lavage from exposed mice. Topical application of Magnesium Aluminum Silicate to human skin daily for 1 week produced no adverse effects. Occupational exposure to mineral dusts has been studied extensively. Fibrosis and pneumoconiosis have been documented in workers involved in the mining and processing of Aluminum Silicate, Calcium Silicate, Zirconium Silicate, Fuller's Earth, Kaolin, Montmorillonite, Pyrophyllite, and Zeolite. The Cosmetic Ingredient Review (CIR. The Cosmetic Ingredient Review (CIR) Expert Panel concluded that the

Related articles

Review Final report of the safety assessment of L-Ascorbic Acid, Calcium Ascorbate, Magnesium [Int J Toxicol. 2005]

Review Safety assessment of Salicylic Acid, Butyloctyl Salicylate, Calcium Salicylate, C12-15 Alkyl Salicylate, [Int J Toxicol. 2003]

Review Final report on the safety assessment of potassium silicate, sodium metasilicate, and sodium [Int J Toxicol. 2005]

Review Final report of the safety assessment of Alcohol Denat., including SD Alcohol 3-A, SD Alcohol [Int J Toxicol. 2008]

Review Final report on the safety assessment of capsicum annuum extract, capsicum annuum fruit [Int J Toxicol. 2007]

» See reviews... | » See all...

Patient Drug Information

Penicillin G Potassium or Sodium Injection (Pfizerpen®) Your doctor has ordered penicillin, an antibiotic, to help treat your infection. The drug will be

Lithium (Eskalith CR®, Eskalith®, Lithobid®) Lithium is used to treat and prevent episodes of mania (frenzied, abnormally excited mood) in people with

Source: AHFS Consumer Medication Information

Recent Activity

Turn Off Clear

Final report on the safety assessment of aluminum silicate, calcium silicate, magnesium

extensive pulmonary damage in humans was the result of direct occupational inhalation of the dusts and noted that lesions seen in animals were affected by particle size, fiber length, and concentration. The Panel considers that most of the formulations are not respirable and of the preparations that are respirable, the concentration of the ingredient is very low. Even so, the Panel considered that any spray containing these solids should be formulated to minimize their inhalation. With this admonition to the cosmetics industry, the CIR Expert Panel concluded that these ingredients are safe as currently used in cosmetic formulations. The Panel did note that the cosmetic ingredient, Talc, is a hydrated magnesium silicate. Because it has a unique crystalline structure that differs from ingredients addressed in this safety assessment, Talc is not included in this report.

PMID: 12851164 [PubMed - indexed for MEDLINE]

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Exhibit 16

U.S. Food and Drug Administration

Department of Health and Human Services

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TITLE 21--FOOD AND DRUGS
CHAPTER I--FOOD AND DRUG ADMINISTRATION
DEPARTMENT OF HEALTH AND HUMAN SERVICES

SUBCHAPTER E--ANIMAL DRUGS, FEEDS, AND RELATED PRODUCTS

PART 582 SUBSTANCES GENERALLY RECOGNIZED AS SAFE

§ 582.1125 - Aluminum sulfate.
§ 582.1127 - Aluminum ammonium sulfate.
§ 582.1129 - Aluminum potassium sulfate.
§ 582.1131 - Aluminum sodium sulfate.
§ 582.1135 - Ammonium bicarbonate.
§ 582.1137 - Ammonium carbonate.
§ 582.1139 - Ammonium hydroxide.
§ 582.1141 - Ammonium phosphate.
§ 582.1143 - Ammonium sulfate.
§ 582.1155 - Bentonite.
§ 582.1165 - Butane.
§ 582.1191 - Calcium carbonate.
§ 582.1193 - Calcium chloride.
§ 582.1195 - Calcium citrate.
§ 582.1199 - Calcium gluconate.
§ 582.1205 - Calcium hydroxide.
§ 582.1207 - Calcium lactate.
§ 582.1210 - Calcium oxide.
§ 582.1217 - Calcium phosphate.
§ 582.1235 - Caramel.
§ 582.1240 - Carbon dioxide.
§ 582.1275 - Dextrans.
§ 582.1320 - Glycerin.
§ 582.1324 - Glyceryl monostearate.
§ 582.1355 - Helium.
§ 582.1366 - Hydrogen peroxide.
§ 582.1400 - Lecithin.
§ 582.1425 - Magnesium carbonate.
§ 582.1428 - Magnesium hydroxide.
§ 582.1431 - Magnesium oxide.
§ 582.1480 - Methylcellulose.
§ 582.1500 - Monoammonium glutamate.
§ 582.1516 - Monopotassium glutamate.
§ 582.1540 - Nitrogen.
§ 582.1585 - Papain.
§ 582.1613 - Potassium bicarbonate.
§ 582.1619 - Potassium carbonate.
§ 582.1625 - Potassium citrate.
§ 582.1631 - Potassium hydroxide.
§ 582.1643 - Potassium sulfate.
§ 582.1655 - Propane.
§ 582.1666 - Propylene glycol.
§ 582.1685 - Rennet.
§ 582.1711 - Silica aerogel.
§ 582.1721 - Sodium acetate.
§ 582.1736 - Sodium bicarbonate.
§ 582.1742 - Sodium carbonate.
§ 582.1745 - Sodium carboxymethylcellulose.
§ 582.1748 - Sodium caseinate.
§ 582.1751 - Sodium citrate.

- § 582.1763 - Sodium hydroxide.
- § 582.1775 - Sodium pectinate.
- § 582.1778 - Sodium phosphate.
- § 582.1781 - Sodium aluminum phosphate.
- § 582.1792 - Sodium sesquicarbonate.
- § 582.1804 - Sodium potassium tartrate.
- § 582.1810 - Sodium tripolyphosphate.
- § 582.1901 - Triacetin.
- § 582.1973 - Beeswax.
- § 582.1975 - Bleached beeswax.
- § 582.1978 - Carnauba wax.

Subpart C--Anticaking Agents

- § 582.2122 - Aluminum calcium silicate.
- § 582.2227 - Calcium silicate.
- § 582.2437 - Magnesium silicate.
- § 582.2727 - Sodium aluminosilicate.
- § 582.2729 - Hydrated sodium calcium aluminosilicate.
- § 582.2906 - Tricalcium silicate.

Subpart D--Chemical Preservatives

- § 582.3013 - Ascorbic acid.
- § 582.3021 - Benzoic acid.
- § 582.3041 - Erythorbic acid.
- § 582.3081 - Propionic acid.
- § 582.3089 - Sorbic acid.
- § 582.3109 - Thiodipropionic acid.
- § 582.3149 - Ascorbyl palmitate.
- § 582.3169 - Butylated hydroxyanisole.
- § 582.3173 - Butylated hydroxytoluene.
- § 582.3189 - Calcium ascorbate.
- § 582.3221 - Calcium propionate.
- § 582.3225 - Calcium sorbate.
- § 582.3280 - Dilauryl thiodipropionate.
- § 582.3336 - Gum guaiac.
- § 582.3490 - Methylparaben.
- § 582.3616 - Potassium bisulfite.
- § 582.3637 - Potassium metabisulfite.
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- § 582.3660 - Propyl gallate.
- § 582.3670 - Propylparaben.
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- § 582.3784 - Sodium propionate.
- § 582.3795 - Sodium sorbate.
- § 582.3798 - Sodium sulfite.
- § 582.3845 - Stannous chloride.
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§ 582.3890 - Tocopherols.

Subpart E--Emulsifying Agents

§ 582.4101 - Diacetyl tartaric acid esters of mono- and diglycerides of edible fats or oils, or edible fat-forming fatty acids.
§ 582.4505 - Mono- and diglycerides of edible fats or oils, or edible fat-forming acids.
§ 582.4521 - Monosodium phosphate derivatives of mono- and diglycerides of edible fats or oils, or edible fat-forming fatty acids.
§ 582.4666 - Propylene glycol.

Subpart F--Nutrients and/or Dietary Supplements[1]

§ 582.5013 - Ascorbic acid.
§ 582.5017 - Aspartic acid.
§ 582.5049 - Aminoacetic acid.
§ 582.5065 - Linoleic acid.
§ 582.5118 - Alanine.
§ 582.5145 - Arginine.
§ 582.5159 - Biotin.
§ 582.5191 - Calcium carbonate.
§ 582.5195 - Calcium citrate.
§ 582.5201 - Calcium glycerophosphate.
§ 582.5210 - Calcium oxide.
§ 582.5212 - Calcium pantothenate.
§ 582.5217 - Calcium phosphate.
§ 582.5223 - Calcium pyrophosphate.
§ 582.5230 - Calcium sulfate.
§ 582.5245 - Carotene.
§ 582.5250 - Choline bitartrate.
§ 582.5252 - Choline chloride.
§ 582.5260 - Copper gluconate.
§ 582.5271 - Cysteine.
§ 582.5273 - Cystine.
§ 582.5301 - Ferric phosphate.
§ 582.5304 - Ferric pyrophosphate.
§ 582.5306 - Ferric sodium pyrophosphate.
§ 582.5308 - Ferrous gluconate.
§ 582.5311 - Ferrous lactate.
§ 582.5315 - Ferrous sulfate.
§ 582.5361 - Histidine.
§ 582.5370 - Inositol.
§ 582.5375 - Iron reduced.
§ 582.5381 - Isoleucine.
§ 582.5406 - Leucine.
§ 582.5411 - Lysine.
§ 582.5431 - Magnesium oxide.
§ 582.5434 - Magnesium phosphate.
§ 582.5443 - Magnesium sulfate.
§ 582.5446 - Manganese chloride.
§ 582.5449 - Manganese citrate.

§ 582.5452 - Manganese gluconate.
§ 582.5455 - Manganese glycerophosphate.
§ 582.5458 - Manganese hypophosphite.
§ 582.5461 - Manganese sulfate.
§ 582.5464 - Manganous oxide.
§ 582.5470 - Mannitol.
§ 582.5475 - Methionine.
§ 582.5477 - Methionine hydroxy analog and its calcium salts.
§ 582.5530 - Niacin.
§ 582.5535 - Niacinamide.
§ 582.5580 - D-Pantothenyl alcohol.
§ 582.5590 - Phenylalanine.
§ 582.5622 - Potassium chloride.
§ 582.5628 - Potassium glycerophosphate.
§ 582.5634 - Potassium iodide.
§ 582.5650 - Proline.
§ 582.5676 - Pyridoxine hydrochloride.
§ 582.5695 - Riboflavin.
§ 582.5697 - Riboflavin-5-phosphate.
§ 582.5701 - Serine.
§ 582.5772 - Sodium pantothenate.
§ 582.5778 - Sodium phosphate.
§ 582.5835 - Sorbitol.
§ 582.5875 - Thiamine hydrochloride.
§ 582.5878 - Thiamine mononitrate.
§ 582.5881 - Threonine.
§ 582.5890 - Tocopherols.
§ 582.5892 - a-Tocopherol acetate.
§ 582.5915 - Tryptophane.
§ 582.5920 - Tyrosine.
§ 582.5925 - Valine.
§ 582.5930 - Vitamin A.
§ 582.5933 - Vitamin A acetate.
§ 582.5936 - Vitamin A palmitate.
§ 582.5945 - Vitamin B[bdi1][bdi2].
§ 582.5950 - Vitamin D[bdi2].
§ 582.5953 - Vitamin D[bdi3].
§ 582.5985 - Zinc chloride.
§ 582.5988 - Zinc gluconate.
§ 582.5991 - Zinc oxide.
§ 582.5994 - Zinc stearate.
§ 582.5997 - Zinc sulfate.

Subpart G--Sequestrants[2]
§ 582.6033 - Citric acid.
§ 582.6085 - Sodium acid phosphate.
§ 582.6099 - Tartaric acid.
§ 582.6185 - Calcium acetate.
§ 582.6193 - Calcium chloride.
§ 582.6195 - Calcium citrate.

- § 582.6197 - Calcium diacetate.
- § 582.6199 - Calcium gluconate.
- § 582.6203 - Calcium hexametaphosphate.
- § 582.6215 - Monobasic calcium phosphate.
- § 582.6219 - Calcium phytate.
- § 582.6285 - Dipotassium phosphate.
- § 582.6290 - Disodium phosphate.
- § 582.6386 - Isopropyl citrate.
- § 582.6511 - Monoisopropyl citrate.
- § 582.6625 - Potassium citrate.
- § 582.6751 - Sodium citrate.
- § 582.6754 - Sodium diacetate.
- § 582.6757 - Sodium gluconate.
- § 582.6760 - Sodium hexametaphosphate.
- § 582.6769 - Sodium metaphosphate.
- § 582.6778 - Sodium phosphate.
- § 582.6787 - Sodium pyrophosphate.
- § 582.6789 - Tetra sodium pyrophosphate.
- § 582.6801 - Sodium tartrate.
- § 582.6804 - Sodium potassium tartrate.
- § 582.6807 - Sodium thiosulfate.
- § 582.6810 - Sodium tripolyphosphate.
- § 582.6851 - Stearyl citrate.

Subpart H--Stabilizers

- § 582.7115 - Agar-agar.
- § 582.7133 - Ammonium alginate.
- § 582.7187 - Calcium alginate.
- § 582.7255 - Chondrus extract.
- § 582.7330 - Gum arabic.
- § 582.7333 - Gum ghatti.
- § 582.7339 - Guar gum.
- § 582.7343 - Locust bean gum.
- § 582.7349 - Sterculia gum.
- § 582.7351 - Gum tragacanth.
- § 582.7610 - Potassium alginate.
- § 582.7724 - Sodium alginate.

Authority: 21 U.S.C. 321, 342, 348, 371.
Source: 41 FR 38657, Sept. 10, 1976, unless otherwise noted.

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AOCS Mission Statement
To be a forum for the exchange of ideas, information and experience among those with a professional interest in the science and technology of fats, oils and related substances in ways that promote personal excellence and provide for a high standard of quality.

Exhibit 17

Bleaching and Purifying Fats and Oils

Theory and Practice

H.B.W. Patterson

AOCS PRESS

Champaign, Illinois

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Preface

The title of this book has been chosen so as to emphasize that some major operations traditionally named bleaching are much wider in scope than the mere removal of color. The selective removal of unwanted nonfat minor components from the parent fat is a form of separation which may be taken to include, in some cases, their destruction or chemical modification. Sometimes the process step is directed principally at the removal of pigment, but removes other minor components as a bonus. In other cases, the removal of components such as remaining traces of gums, soaps, poisons of hydrogenation catalysts and pro-oxidant metals is the prime consideration; hence, we speak of purifying. Damage to the parent fat has to be avoided, and this relates to its intended use. A procedure employed in preparation of a technical or nonedible product may be quite unacceptable for edible material.

The different physical and chemical operations now in use for bleaching and purifying are described in detail from a practical standpoint. Adsorption is a major technique; the way it works has come to be better understood as instruments and methods of analysis have grown more sensitive. The theory of their operation and the structure and manufacture of adsorbent earths and carbons are simply explained for the benefit of processors already working in the fats and oils industry and for those entering it. The special use of adsorbent silica is also described, as well as other techniques. The chemical nature of the unwanted components is given; this serves to distinguish them from the fats in which they are found. It is against this background that the processing of some twenty of the most important fats or oils is considered individually.

Separate chapters deal with bleachers and filters—not forgetting the vitally important filter membranes. Finally, oil recovery, safety matters and the significance of commonly used tests are considered where these have particular relevance to the subject.

As with two earlier books, the author is much indebted to the painstaking work of Mrs. Marjorie Honor, who prepared the text during the years of its composition.

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Chapter 2

Adsorption

Physical Adsorption and Chemisorption

Adsorption is a phenomenon wherein the local concentration of a substance at the surface of a solid or liquid becomes greater than the concentration throughout the bulk. We thus have the well-known phenomena of gas molecules concentrating on charcoal or pigments passing from solution in oil to deposit on clay. By contrast, absorption relates to the uniform penetration and dispersal of one item into another. For example, hydrogen rapidly penetrates and dissolves in palladium, light of a particular wavelength is taken up by a layer of liquid and gases are selectively removed from an air stream by droplets of a scrubbing liquid.

It has been concluded that solute molecules which reduce surface tension will concentrate at an interface between a solid and a solution and tend to be adsorbed on the solid. If, as happens in some cases, the solute increases surface tension, the concentration at the interface is diminished; this is known as negative adsorption. Water has a high surface tension; most solutes reduce this, so they are easily taken up by an adsorbent. Alcohol has a substantially lower surface tension than water, so most solutes are less able to lower it appreciably. Hence they are not as readily adsorbed from alcoholic solution. This thermodynamic aspect of adsorption is treated in textbooks of physical chemistry under the heading of the Gibbs adsorption equation.

When it comes to a question of the adsorption of gases on a solid, two types of forces are considered to be operating. Weak forces attracting the gas molecules to the solid surface are seen to be of the same kind as those holding the molecules together when the gas is in the liquid state. It is notable that heats of adsorption and heats of condensation are broadly similar and relatively low. These weak forces are referred to as van der Waals forces and promote a physical adsorption. They are most in evidence at low and moderately low temperatures. It is not surprising that gases which are most easily adsorbed are also most easily liquefied. Put in another way, the volumes of gases adsorbed by a set weight of charcoal in moderate conditions such as 15°C and 1 atm are found to be in the same order as their boiling points, with much more chlorine, hydrogen sulphide or ammonia being adsorbed

than carbon monoxide or oxygen. This weak physical adsorption is reversible at the same temperature simply by lowering the pressure.

A second type of adsorption depends upon forces of chemical attraction between the surface and the surrounding gases or solute molecules in a surrounding liquid. This is called chemisorption. It is less common than physical adsorption; when it occurs the heat of adsorption may be ten or more times greater. It is most in evidence at moderate temperatures, and to reverse it a considerable rise in temperature is needed. If a mixture of hydrogen sulphide and oxygen passes over charcoal at room temperature, the hydrogen sulphide is adsorbed much more strongly. This is because the sulphur end of the H_2S molecule is more negative than the hydrogen. That is, the molecule is polar, whereas the oxygen molecule is symmetrical and nonpolar. If, however, the temperature is markedly lowered, van der Waals forces come into play and even nonpolar molecules are adsorbed. Oxygen is strongly adsorbed at $-196°C$. Furthermore, it appears likely that molecules of a gas such as hydrogen may dissociate to atoms when adsorbed on the surface of metals such as nickel and copper. As is well known, this condition facilitates their attack on the carbon–carbon double bonds in a surrounding liquid such as an unsaturated oil.

As early as 1908 it was suggested (156) that two mechanisms of adsorption operated together, one being electrochemical (chemisorption) and the other physical adsorption. Seemingly, once chemisorption has created a unimolecular layer on the surface available for that effect, the weaker van der Waals forces may make some further addition, depending in part upon the concentration of pigment remaining in solution.

Various investigators have approached the bleaching effect of activated clays as being partly an ion exchange mechanism (159). In the bleaching and purifying of fats and oils with adsorbents such as clays, carbon and special silica, van der Waals and chemical forces can play a part. This depends upon the adsorbent, the nature of the minor component intended to be removed (the adsorbate) and the conditions of their contact. This brief exposition of the nature of adsorption should make clear that is is a complex phenomenon.

Adsorption Efficiency and Variation

Chemical valency-type attraction falls off rapidly with distance, so it is likely to be responsible for only one layer of adsorbed molecules, whereas the van der Waals forces, though themselves weak, are considered capable of being exerted from the first layer to attract a further layer and so on, to several layers, especially if the temperature is fairly low and pressure rather high. In 1916 Langmuir advanced a mathematical relation which related the extent of adsorption of a gas to the pressure for any constant temperature (the Langmuir isotherm). Assuming the layer of adsorbed molecules does not exceed one molecule in thickness, an equilibrium is reached for any particular pressure between molecules evaporating from the surface (related to how much is already covered) and the molecules condensing onto it (related to the unoccupied space left available). At low pressures (lots of unoccupied space) the amount adsorbed per unit mass of adsorbent closely follows the pressure exerted. At the other extreme, as the surface becomes almost completely covered by a unimolecular layer, the amount adsorbed per unit mass approaches a constant limiting value at any temperature as pressure increases. At low temperatures (well below 0°C) this limit is approached gradually; at normal and higher temperatures (above 0°C) the limit is approached quite quickly. This unimolecular layer is a necessary condition for the fulfillment of the Langmuir isotherm. Many instances have been found where it is followed closely; where there are deviations, one reason could be the intrusion of the weak van der Waals forces.

In the coverage of the surface which is intermediate between the two extremes just described, an empirical mathematical relationship provides a useful description for practical purposes of the relation between the extent of adsorption per unit mass of adsorbent and the pressure of surrounding gas molecules or concentration of solute molecules in a solvent. This is known as the Freundlich isotherm because, although not its inventor, he used it frequently to interpret his findings on the adsorption of solutes from solutions. This expression also applies to adsorption from colloidal dispersion. Although different textbooks vary slightly in their terminology, a popular expression of the Freundlich isotherm is

$$\frac{x}{m} = Kc^n$$

where x = amount of substance adsorbed (adsorbate)
m = amount of adsorbent
c = concentration of substance remaining unabsorbed
K = a constant relating to the general capacity of that adsorbent for that adsorbate
n = a constant relating to the manner in which the efficiency of adsorption changes as it progresses from higher to lower color. Some authors write the value as $1/n$, but regardless of the notation, the numerical value of the index ranges in effect between approximately 0.1 and 1.0.

It follows that

$$\log \frac{x}{m} = \log K + n \log C$$

The implications of this relationship for practical purposes have been clearly illustrated (127,155) as shown in Fig. 2-1. Plotted on a log-log scale, the isotherms (within the limits for the test sequences) come close to forming a straight line, as was expected. By convention, the slope of any line is n and the intercept is K. The concentration of pigment is measured in Lovibond color units. The value of the equation is independent of the particular color measurement chosen as long as the results are additive.

The following implications may be drawn.

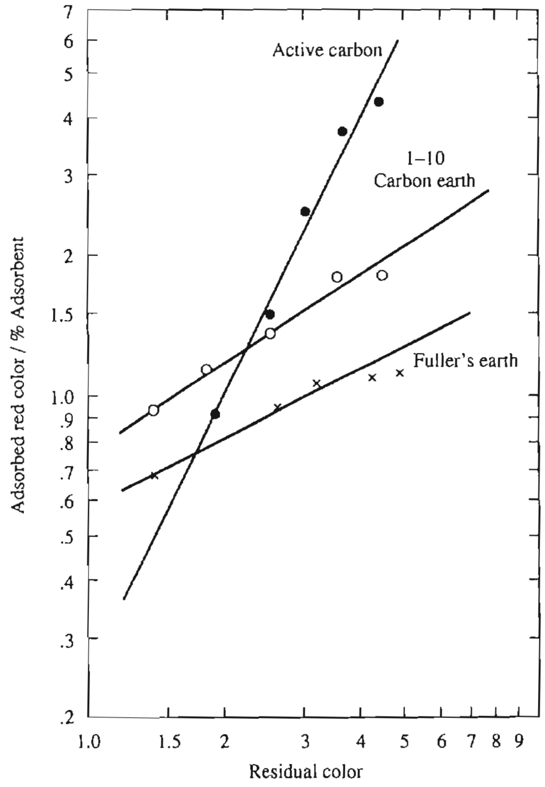


Fig. 2-1. Bleaching of refined cottonseed oil (25Y-5,5R).

1. Where K is larger, less of that adsorbent is needed to achieve the lower color in question. This means the adsorbent tolerates a larger amount of pigment being taken up in lowering the final color (residual unadsorbed pigment). Thus for a final color of 1.0 in Fig. 2-1, the carbon–earth mixture is rather more efficient than the Fuller's earth, but both are more efficient than carbon.
2. The index n relates to the rate of change in adsorption efficiency as bleaching progresses. Carbon tolerates a high load of pigment if the final residual color need not be low, but its efficiency drops rapidly as a low final color is sought. This suggests a modest amount of carbon in mixture with earth will effectively lower the color as bleaching commences, after which the earth is even better placed to continue the process and reach the required lower level. This means K for the mixture is raised because the whole isotherm is lifted by early removal of color by the carbon component.
3. It is obvious from the previous statements that in selecting an adsorbent it is vital to recognize over what range of removal of color—or other component—it is intended to operate. Equally, if two adsorbents are being compared, the comparison should be over the same range. Low values for n indicate the slope of the isotherm is low and the performance does not change quickly across the range.

It is worth emphasizing that in reaching these results, no gross competition from soap, gums and so forth is being experienced and that comparisons are made at the same operating temperature, moisture content, absence of air and so forth. Also, K and n values hold good for a particular adsorbate–adsorbent (color–clay) system and will show differences for other tasks and at other temperatures.

If we look at the results obtained at extreme conditions where there is a departure from the theoretical Freundlich isotherm, the reasons for the divergence are not difficult to identify. For example, when the concentration of clay is already high and the color has become light, the amount of bleaching achieved by use of an even greater clay dose falls rapidly. This means the low concentration of pigment remaining in solution is able to be in equilibrium with a low concentration of pigment on the large dose of that particular clay.

At the opposite extreme of high loading of pigment onto the surface of a small clay dose, this loading could be rather higher if other minor components were not interfering by competing with the pigment for adsorption. As the dose is increased this interference is overcome and the color lightens as the dose increases in accordance with the Freundlich isotherm. Finally, the extreme of very large clay dosage just described is reached. There is evidence, at least in several instances, that there is adsorption from solution which leads to the formation of a single layer of solute molecules on the surface of the solid adsorbent; this is closely analogous to chemisorption of a gas as was mentioned earlier. It is, therefore, to be expected that an equation similar to the Langmuir isotherm should describe the effect of concentration on the extent of adsorption from solution. By replacing gas pressure by concentration of solute in solution we obtain the equivalent of the Langmuir isotherm (156,157)

$$\frac{C}{(x/m)} = \frac{1}{a \cdot b} + \frac{C}{a}$$

where C = concentration of substance remaining unabsorbed
x = amount of substance adsorbed
m = amount of adsorbent
a = a constant giving a measure of the surface area of the adsorbent
b = a constant giving a measure of the intensity of adsorption

Taking various predetermined amounts of rubber seed oil and melon seed oil in many bleaching tests and working with Fuller's earth, activated carbon and a mixture (1:1) of these at 30°, 55° and 80°C, Achife and Ibemesi (157) found good agreement with Freundlich and Langmuir isotherms as were previously expressed. It was concluded adsorption of the pigments proceeded by formation of monolayers on the surface of the adsorbent. The following conclusions were drawn from the experiments:

1. The specific adsorption (x/m) increased with oil concentration (*i.e.*, higher oil to adsorbent ratios). This was taken to signify an increase in collision frequency between molecules of pigment and adsorbent, but this effect reached a maximum and then declined, possibly due to oil molecules competing with pigment for adsorption.
2. For both oils and all three adsorbents, a clear increase in specific adsorption was noted with increase in temperature within the moderate temperature range investigated. This was attributed to activation of more adsorption sites arising from increased porosity and total pore volume at the higher temperatures. This improvement depended mostly upon the structure of the adsorbent, since it was clearly more pronounced with one adsorbent (Fuller's earth) than another (activated carbon). The effect was also more obvious with the rubber seed oil than with the melon seed oil.

3. The value of $1/a$ decreased with rise in temperature, again suggesting an increase in active adsorptive surface area as temperature increased.

The adsorption of pure β-carotene from acetone solution by a variety of adsorbents was chosen as the means of studying adsorption phenomena because bleaching of palm oil has become a very large-scale operation in recent years (158). Silica and kaolin were found to be of comparable activity, Fuller's earth about ten times more active and the activated bleaching clay Tonsil much more active than Fuller's earth. It was noted with Tonsil and Fuller's earth that the orange red of carotenoids with adsorption peaks at 478, 453 and 430 nm gave way to peaks at 360 and 330 nm, while the supernatant solution became green. This indicated more than physical adsorption had occurred. With silica the peak at 453 nm decreased, but without any increase at 330 and 360 nm. This suggests only physical adsorption had occurred. Samples of the four adsorbents were each heated in air for 4 h at 150°, 400° and 600°C. Taking the activity of an unheated sample as one, the Tonsil showed activities of 1:3:9:5, the Fuller's earth 1:1:7:7, the kaolin 1:1:2:2 and the silica 1:1:1:0.5. Since these adsorbents were calcined at *ca.* 500°C in the course of manufacture it is to be expected that heating above that temperature could cause structural damage. The improvement at 400°C was seen as being principally due to driving off excess water and burning off organic matter to expose active sites. It apparently did not increase surface area. This interpretation raises the question of how excessive the excess moisture was in the untreated adsorbents, as a small amount is generally considered beneficial (225,226). The fact that heat pretreatment did not improve the silica at any stage was seen as an indication that its adsorptive effect was solely physical and did not involve chemisorption. Further experiments suggested that after an initial very rapid physical adsorption of β-carotene from acetone solution onto the surface of Tonsil, a steady adsorption of more β-carotene proceeded as a first-order chemisorption reaction and this increased in rate when performed at higher temperatures. Finally, it was demonstrated that β-carotene can be destroyed by the presence of ferric ions, even when oxygen is rigorously excluded. Both Tonsil and Fuller's earth gave positive results when tested on this oxygen-free basis.

Conditions Affecting Adsorption

It has already been shown that the progress of adsorption depends in the first place upon the characters of the adsorbent and the adsorbate. With some combinations the interaction may be nil and for others the result is highly favorable. Next comes the important question as to the effect of conditions in which the contact is made. At once it becomes evident that compromises have to be made between securing a favorable effect in one or more respects, such as removal of color, soap, gums and so forth, and doing damage to the oil itself or some minor component. Cost effectiveness is another aspect which must always be kept in mind along with technical efficiency. The requirements can vary considerably in going from one oil to another (*e.g.*, palm to soy oil, tallow to olive oil). It is best to consider the general effect of each important factor in turn and note where they interact with one another, favorably or otherwise.

Temperature

Since several factors are at work in the phenomenon of adsorption, and more still if removal of pigment is the particular operation underway, it is not surprising that a balance must be struck between conflicting influences. We need to distinguish between the effect of a rise in temperature on the adsorptin process itself and the possible destruction, formation or stabilization of color, which may be from the independent effect of heat itself (see sections beginning on pp. 7, 8 and 54).

For simple physical adsorption, van der Waals forces, at a readily accessible surface, temperatures lower than 100°C probably favor the equilibrium condition in which a larger amount of pigment—or other adsorbate—is retained. As the temperature rises above 100°C van der Waals forces are increasingly disrupted, and this may be only slightly compensated by the viscosity of the oil falling and pores expanding so as to create better access to the surface. As for chemisorption, an increase in temperature above 100°C helps to activate sites where it occurs. Where the chemical destruction of pigment is catalyzed by the adsorbent, as with acid activated clays, this becomes an important factor as the temperature rises above 120°C. Other effects become noticeable above 95°C, especially with acid activated clays, splitting of soap if present and some triglyceride to form free fatty acid is detectable. When the temperature is raised toward 160°C structural alteration of polyunsaturated fatty acids is likely (*e.g.*, migration of double bonds). Finally, it is pertinent to recall (see p. 20) that when a good quality crude whale oil was to be extensively polymerized for use as a component of wool combing oil or a soft oil in soap manufacture, it would first be given a 2% activated clay bleach and then raised to 300°C while a current of steam passed through the oil under reduced pressure, thus excluding air. In these circumstances color improved and viscosity increased during polymerization. The same effect can be achieved with fish oil, but in this case a preliminary alkali neutralization, washing and clay bleaching is needed if the color is to lighten rather than darken at 300°C. This clearly indicates the necessity of removing mucilage before the high temperature treatment; other findings agree (176).

A very detailed investigation (136) of atmospheric bleaching based upon neutralized cottonseed oil and neutralized soybean oil was reported in 1949. Those natural or so-called neutral bleaching clays examined achieved their maximum color removal between 118–132°C. The various commercial activated clays performed best in the narrow band 100–106°C. The use of temperatures above 106°C in air served only to increase the well-known catalytic prooxidant action of the acid activated clays; the net effect of this oxidation was an increasingly poorer color because the point had been reached where formation and stabilization of new color exceeded bleaching of original color. Some adsorbents containing a particularly high proportion of silica needed to be heated to *ca.* 200°C to achieve their maximum effect of color removal, evidently because they exerted no catalytic pro-oxidant influence. This high temperature obviously stands in the way of their use for edible oil air bleaching because of inevitable oxidation and damage to the fat itself. Certainly, for edible oil bleaching using adsorbents vacuum is the normal practice, and 95–105°C is also normal for optimum results. Another study (125) confirms this, and yet a further study (29) makes it clear that if color removal is the only criterion and the pigment present oxidizes readily without significant catalytic help, a neutral clay may prove moderately more effective than an activated one, provided new color is not formed or color fixed. This would apply to an inferior tallow containing some carotenoid-type pigment but not to the removal of chlorophylls, which is more dependent on true adsorption.

Duration

Discussion of what constitutes an adequate contact time between oil and adsorbent presupposes sufficient agitation. In the case of the conventional gate stirrer of batch bleachers an rpm of *ca.* 40 suffices, or its equivalent in terms of sparger steam. Excessive agitation wastes power and may increase incorporation of air. More than half the color is likely to be adsorbed in the first 5 min, and after 15 min further improvement is slight. When we are primarily concerned with the adsorption of other minor components such as gums, soaps and so forth, the same holds true. An increase in temperature quickens initial adsorption; prolongation of contact in the bleacher beyond 30 min favors color reversion. As pointed out in the discussion of batch bleaching (see

p. 49), there is contact with a massive concentration of clay in oil lasting for up to a few minutes in passing through the clay layers of a filter unit. Where oil is bleached as a solvent miscella there is a rapid fall in color during the first few minutes. For more information, refer to individual studies (29,110,125,136,137,141,158,162,163,225,226). In several of these it is important to note whether the author is talking about atmospheric or vacuum bleaching. Conditions of contact, time and temperature for special adsorbent silicas are broadly the same as for clays.

Dosage

It has been explained (see section beginning on p. 61) that the efficiency of a particular bleaching clay is related to the severity of the task given to it. A clay which readily takes up pigment when plenty is available may have to be used in very large doses if a very light final color is demanded. This means the relative efficiency of two clays may even be reversed as a lower color is achieved.

When it comes to removal or destruction of components other than pigments there can be similar wide differences; for example, a silica which is highly efficient in removing gums and soap can be useless for removal of chlorophyll. An adsorbent should be chosen for factory use as a result of a practical test in the same circumstances and to the standard of its full-scale use. It may also happen that having discovered the dose required to cope with a parcel of oil that is more difficult than usual to bleach, this becomes the routine factory practice for all oil of that species. Over months this is very wasteful of clay, oil lost in clay, and plant and labor utilization. This neglect is the very opposite of the practice of making good use of the press bleaching effect, in which dosage is decreased as the filter acquires an increasingly thick coating of adsorbent.

The performance of three clays from the same manufacturer when bleaching soybean and canola oils is shown in Fig. 2-2 (141). Comparable isotherms exist for the removal of red color from the same two oils.

A more subtle point emerges when we consider the clay dosage in relation to future oxidative stability, not only for the bleached oil but also for the same oil after deodorization. Figure 2-3 (100) shows in the cases of both activated clay Gr 105 and the more highly activated Gr 160 that when bleaching soybean oil of original PV 6.9, the PV had dropped well below 1.0 by the time the AnV was in decline. This leads to the reasonable deduction that the catalytic decomposition of the peroxides is preferred over the adsorption of aldehydes at the active sites of the clay.

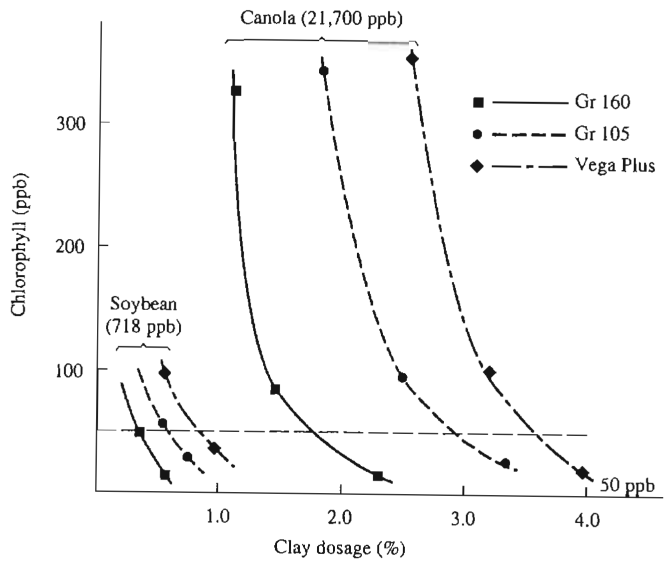


Fig. 2-2. Bleached oil chlorophyll adsorption isotherms in soybean and medium chlorophyll canola.

Of particular interest is the observation that when the fall in color (Lovibond red or chlorophyll) is plotted against dosages of the same clays it also becomes clear that adsorption of pigments is preferred over the adsorption of aldehydes, a large part of which takes place after most of the pigments have been removed. This leads to the important conclusion that at a dosage level where colors are removed to acceptable levels, the oil can still have a poor oxidative stability (*i.e.*, high in aldehydes). The study was continued to the point where the Totox value (2 PV + AnV) of the bleached oil was compared with the clay dosage (upper Fig. 2-4) (100); then the Totox value of the bleached-deodorized oil was compared with the clay dosage (lower Fig. 2-4) (100).

Plotting bleached-deodorized oil Totox against bleached oil Totox gave a clear linear relationship (141); when the bleached Totox was 2.0 the deodorized was 1.0, and when the bleached Totox reached 12.0 the deodorized Totox became 6.0. If the policy is to produce deodorized oils of no more than Totox 3.0, the previously explained type of control suggests a way to achieve it. Less expected was the result (141) that if clay dosages were increased well above the level needed to obtain satisfactory color and oxidation values, the oxidative stability began to fall. It is suggested that these excessive doses of activated clay begin to diminish the tocopherol content of the oil to a substantial extent and, therefore, lower the natural resistance to oxidation of the oil. In the investigation (100) of several crude soybean oil feedstocks ranging from 2.0 to 10.0 PV, of which all had relatively low AnV, an increase of activated clay (Gr 160) from 0.2 to 2.0% dosage was needed to ensure that the Totox of the final deodorized oil did not exceed 3.0. Although various soy oil feedstocks were used in the studies just described it seems reasonable that the findings must apply in principle to many oils. It is worth repeating that the steps taken in the early stages of treatment to remove gums, soap and so forth greatly assist the action of the adsorbent to be used later. Secondly, although oxidative stability (chemical test) is not the same as flavor stability (organoleptic assessment), if the former is satisfactory, this goes a long way toward ensuring the latter.

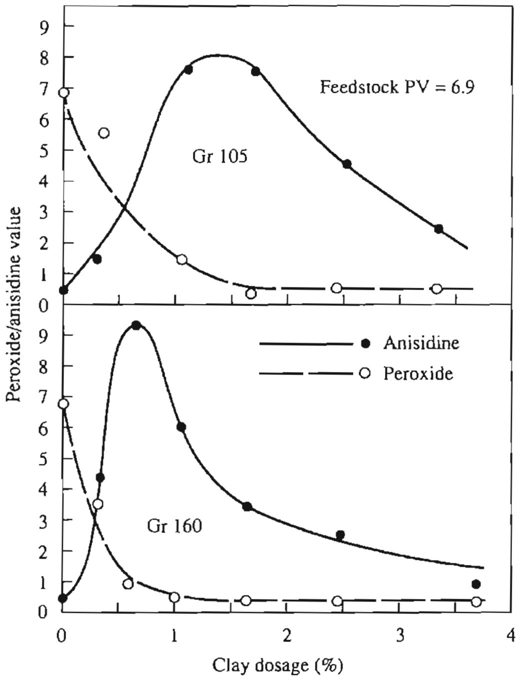


Fig. 2-3. Bleached oil peroxide and anisidine values *vs.* clay dosage.

Atmospheric and Nonatmospheric Bleaching

From what has already been written at the end of the discussion of temperature, in relation to particular features of bleaching in air (see

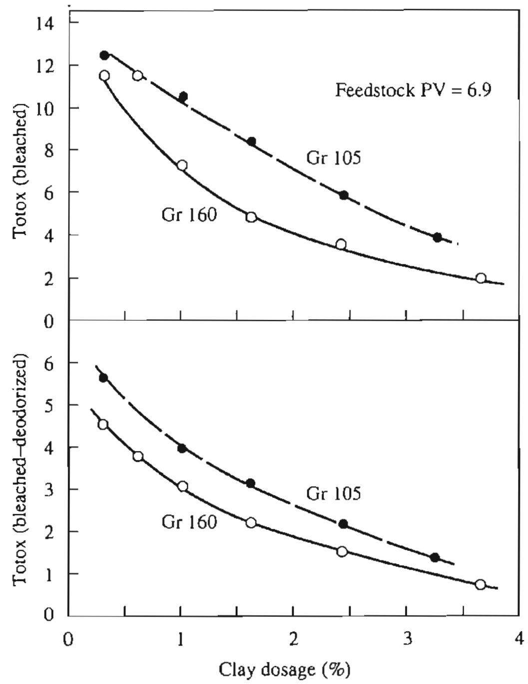


Fig. 2-4. Bleached and bleached-deodorized Totox *vs.* clay dosage.

p. 67) it will be evident that this application is limited to certain nonedible products. The details can be found in several references (29,125, 135,136,141,162,176). The hazards to quality arising from ample contact with air from extraction of the seed to the deodorization of the oil have been reviewed in detail (164).

Some points merit emphasis:

1. By the end of the bleaching cycle oils will have lost some of their natural antioxidant and are then most vulnerable.
2. Activated earths are pro-oxidant catalysts as well as adsorbers of oxidized fat.
3. Air drawn into the oil along with clay and contact between hot filtering oil and air are sources of damage.
4. The polyunsaturated oils are most at risk to oxidation. Reaction between them and dissolved oxygen is extremely rapid (see p. 21).
5. Reaction rates double for approximately each 10°C rise in temperature, so oil and dissolved oxygen will react about 40 times more quickly at 80°C than at 20°C.

6. Open filtration of edible oil after bleaching should be avoided entirely, and if oil is not blanketed by nitrogen during storage this should be kept as short as possible, under eight hours. Unsaturated oils are obviously most at risk. Good filtration discipline will keep the clay content of filtered oil comfortably below 100 ppm.

Moisture

Moisture in the bleaching operation may arise from three sources. First, it may arise from the moisture naturally present in the clay as it is used, secondly, from the oil as it is brought forward to the bleaching operation and third, it may be deliberately added in certain bleaching procedures of technical grade fats (176,225). Usually, activated clays as supplied in temperate climates are in equilibrium with their surroundings at around 10% w/w free moisture. During storage in monsoon conditions this may reach nearly 30%. Activated clays, natural clays and carbon affected in this way are quite able to perform satisfactorily, although it may be prudent in calculating the dosage to make an allowance for the exceptionally high moisture content of the adsorbent. Some manufacturers will state the optimum moisture range (*e.g.*, 15–23% H_2O) for their products for given bleaching tasks (141).

A common practice has been to dry the oil to about 0.1% H_2O w/w before adding bleaching clay. If the oil is to go forward to a dead-end hydrogenation system it is advantageous for it to enter the autoclave not above 0.05% H_2O. This low level cuts down the volatiles in the headspace early in the hydrogenation. Since the clay addition to the oil will be on the order of 1% w/w, the moisture contributed by the clay is insignificant compared with what is appropriate for the oil. Oil which has just been alkali neutralized, washed and settled will hold *ca.* 0.6% H_2O. If, through operator error, adsorbent clay is added to oil whose moisture content is well above this level, the clay may form coarse aggregates. This necessitates prolonged drying before filtration is practical. One study (127) compared two procedures. In the first, once the wash had been separated from the oil, the clay was added immediately to the oil, then drying and bleaching under vacuum proceeded simultaneously. In the second, the oil was first dried under vacuum, then clay added and bleaching completed under vacuum. No significant difference in color was found. Lastly, when low grade fats are being bleached with a mixture of sulphuric acid and Fuller's earth, some further small additions of water during the bleaching cycle (see section beginning on p. 56) may extend the bleaching action to a useful extent.

Although clays may have been heated to 500°C in the course of manufacture, and therefore dehydrated, they will have had the opportunity to re-establish a moisture content before use. It is to be expected that some water will be bound more firmly than the superficial moisture lost at 105°C, and this water is likely to play an important part in chemisorption. It is suggested (29,125) that water molecules are held between layers in the lamellar structure of bleaching clays. If this water is removed by rigorous or sudden drying, a collapse of the layers is encouraged and the bleaching efficiency is appreciably less because the amount of accessible active surface is less. A related point is that clay should be added to oil at a temperature below the boiling point of water at the pressure being employed; thus violent frothing can be avoided. The oil can then displace moisture from between the laminates in a steady fashion as the temperature is raised without loss of bleaching capacity.

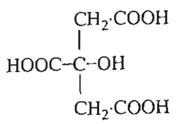
Acidity

How acidity arises in bleaching clays, how it may be enhanced and how this affects adsorption performance are questions intimately related to their structure and activation. The description of these is contained in Chapter 3. At this time it is sufficient to say that natural bleaching clay contains a high proportion of complex aluminum silicate in which a number of other metals such as iron, magnesium, calcium, sodium and potassium are present in varying degrees as impurities. Weathering produces acid-reacting salts such as $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$. Leaching out of the iron or aluminum and substitution of an H cation in effect produces a form of silicic acid, and this, in turn, is capable of donating a proton to the carbon–carbon double bonds present in pigments or other minor components. A carbonium (organic cation) forms. The result is an electrostatic attraction (chemisorption) which holds the adsorbate to the clay.

Acidity is expressed as the titratable acid of a water extract of the clay or as a pH of a suspension of it in water. It has to be noted that in some clays there is considerable buffering effect on the pH from the salts present, so that the obvious inverse relationship between acidity and pH can be disturbed. Hence, two clays of the same acidity (mg KOH/g) may exhibit different pH and vice versa (125). Although activation of clays is highly beneficial with regard to increased bleaching performance, it carries with it certain penalties which must be considered. Such clay will also retain more oil after use. It will more readily split soap and triglyceride to form free fatty acid, it is a more efficient pro-oxidant catalyst and it is more prone to encourage isomerization of unsaturated oil. It is also more expensive. A bonus is its enhanced ability to trap trace metals (29,110,127,141,163).

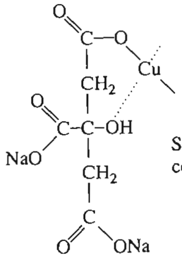
Sequestration

It is important to get rid of pro-oxidant trace metals in refining fats and oils, the most common are iron and copper. Iron at 0.1 ppm and copper at 0.01 ppm can lower the stability of a deodorized oil such as soy oil. Various acids readily combine with these trace metals forming chelate complexes, and this renders the metals inactive as catalysts. Citric acid solution is most popular for this purpose, which is described as sequestration. Other acids which behave in a similar way are ascorbic (vitamin C), phosphoric, tartaric and ethylenediaminetetraacetic (EDTA).



$$\begin{array}{c} CH_2{\cdot}COOH \\ | \\ HOOC{-}C{-}OH \\ | \\ CH_2{\cdot}COOH \end{array}$$

Citric acid



Sodium citrate copper complex

The complexes formed when trace metals are sequestrated are very readily adsorbed by activated clays; hence, this provides a double security. A typical precaution is to add *ca.* 0.05% w/w citric acid/oil as a 50% solution in water to an oil about to be bleached. Some sequestrants do no more than capture trace metals, but others, notably citric acid, will scavenge free oxygen, split soap and convert nonhydratable phosphatides to a hydratable form.

Chemical Side Effects

It has already been explained that the acid condition of activated clays leads to their promoting oxidation, hence the need to bleach in vacuum. Furthermore (see p. 21), activated clays promote the rapid change from hydroperoxy- to hydroxy- to conjugated unsaturation, and this has even been adopted to compare the activity of one clay with another (63). Although more than 100 ppm of activated clay present in an oil as vulnerable as soybean oil after deodorization could exert a damaging pro-oxidant effect, good filtration discipline should easily keep the clay level well below this (see section beginning on p. 17). Any isomeric changes which tend to occur in the absence of air at high deodorization temperatures (230–270°C) will be promoted by the presence of activated clay. Neutral clay does not promote such isomerization. At normal bleaching temperatures (*i.e.*, *ca.* 100°C) neither kind of clay nor carbon cause significant isomerization in the absence of air unless some fat has already been oxidized.

Particle Size (110,126,165,168,225)

Adsorption is by definition a phenomenon related qualitatively to the kind of surface and quantitatively to the extent of that surface. In practice, other requirements are important and make themselves felt through costs. Textbooks give various illustrations of how a cube of an element such as carbon, nickel or sulphur weighing about a gram and having a surface area of a few square centimeters, when divided into particles of 5–10 nm width then has a combined superficial area of around 100 m^2/g or more. Particles of this extremely small size present severe filtration problems. The answer in the case of nickel catalyst is to deposit these nickel crystallite particles throughout the pores of some inert support whose larger porous particles are *ca.* 10,000 nm and above in size. In the case of clays and carbon the basic material is rendered extremely porous by the manufacturing process (Chapter 3), then ground and sieved to a convenient range of particle sizes which no longer pose filtration hazards. Naturally, this process increases cost. In this way commercial activated carbons of 1000 m^2/g are produced. It is atoms sitting on the surface and along the broken edges which have unsatisfied valency bonds and, therefore, it is these same atoms which are most capable of exerting a chemisorptive effect. This is exploited for purposes of bleaching and other forms of purification. A high proportion of pores must be negotiable by adsorbate molecules. A further advantage is that filtration is acceptably rapid when a good proportion of medium-sized particles is present. Complete removal of small particles increases the filtration rate further, but also begins to reduce bleaching activity. This, in turn, increases the necessary dose, hence a compromise gives the optimum result, which translates directly to the final cost. Having overcome the filtration problem by depending more on porosity than small particle size, a different problem is presented by the more porous solids retaining more oil after filtration has been completed. Whereas a natural clay will retain about 30% of its own weight of oil, an activated clay will hold about 70% and activated carbon possibly 150%. Although a useful proportion of these retained oils can be recovered, the cost has to be recognized. Fortunately, for technical reasons explained earlier (see section beginning on p. 42), only a modest proportion of activated carbon is necessary in clay/carbon blends.

Chapter 3

Adsorbents

Mineral Types

A vast amount of research on the nature and action of clays, carbons and synthetic silicas has been completed, especially in the 1980s, which has given us a much better understanding of them as adsorbents and catalysts. Information is given here for those who use them in the processing of fats and oils. For more detailed information on structure and uses, including those outside of the fats and oils field, the several references to excellent original papers should be consulted.

The natural, neutral or nonactivated bleaching clays are derived from clay mineral deposits which are merely dried, milled and sieved to obtain a desired range of particle sizes. Natural weathering over a very long period has rendered the original mineral partly porous and given it some power of adsorption for pigments, soap and so forth. Such material came into early use to cleanse sheepskins from fat (*i.e.*, fulling); therefore, in England it became known as Fuller's earth. This class of material is particularly mild in action, not promoting chemical changes in triglycerides, showing little tendency to split soap and in general responding only modestly when bleached with acid to make it a more active adsorbent.

Throughout the world (with the exception of Antarctica) deposits of different forms of the clay mineral bentonite are found, usually near the surface and in seams up to 15 feet thick. The name bentonite derives from the large deposits associated with Bentonite shale at Rock River, Montana. At least 85% of this material consists of forms of an aluminum silicate known as montmorillonite, which was identified as long ago as 1847 at Montmorillon, France. Basically, montmorillonite is characterized by its three-layer structure. It is composed of a sheet of silica (tetrahedral structure) lying above and below a central sheet of alumina (octahedral structure), hence the description of a 2:1 layered mineral. Electrochemical binding attracts the sheets to one another. Some early explanation of nomenclature is necessary as confusion can easily arise in the minds of nonmineralogists. Subdivisions of this material are of particular interest to organic chemists. First, it is recognized that a divalent magnesium ion (Mg^{+2}) or ferrous ion (Fe^{+2}) may substitute itself for a trivalent aluminum ion (Al^{+3}) in the octahedral layer, and this gives rise to a weak disseminated electronegative charge throughout the layer. In montmorillonite in particular, about one magnesium ion appears for every five aluminum ions. Neutrality and overall stability are restored by positive mobile hydrated alkali cations such as Ca^{+2}, Na^{+} or K^{+} inserting themselves between neighboring triple layers. Because the attraction between the electronegatively charged triple layers and the interlayer positive cations is weak, the neighboring trilayer sheets are able to move slightly apart (expand) and the cations themselves are easily exchangeable by other available cations. This gives rise to the description of swelling bentonite, western (U.S.A.) bentonite and so forth, the replacement cation commonly being sodium and the material having uses as a flocculating or clarification agent (29,141,165,166). The activity of this form of bentonite changes little with acid leaching, and it is not the source of acid activated bleaching earths.

A much more important variant, calcium montmorillonite or nonswelling bentonite [southern (U.S.A.) bentonite, Texas bentonite, *etc.*], lends itself very readily to leaching with mineral acid (HCl or H_2SO_4); its power of adsorption and catalysis are thereby dramatically increased. It is important to add that the entire group of expandable 2:1 layered silicate minerals are classed as smectite, and this term is not confined to montmorillonite. There are other well known 2:1 layered clay minerals incapable of expansion, either because of extremely high layer charge (mica, vermiculite) or no layer charge (talc, pyrophyllite).

Acid activated clays were first produced in Germany around 1905, then several other countries around the world followed; this extension is continuing today. A current approximate world production of 600,000 tons/yr has to be seen against a world production of total bentonite-type minerals of six million tons/yr. The acid activated clays are used in cleaning mineral oils as well as vegetable and animal fats; they are also used as catalysts in promoting organic reactions such as polymerization and isomerization, and may take the form of fixed beds or powdered additions. Finally, they have a role as proton donors in developing color from microencapsulated colorless leuco bases in copy paper (165,167).

Acid Activation and Adsorption of Pigment

As might be anticipated, individual deposits of nonswelling bentonites, although predominantly composed of calcium montmorillonite, show sufficient variation in character to make their acid treatment a matter of judgment by individual manufacturers (168), of whom Süd-Chemie (169), Engelhard, Mizusawa and Laporte are world leaders. (France, Czechoslovakia, India and China also produce considerable amounts of bleaching clays.) For example, one bentonite may rise easily from 100 m^2/g to a peak of 540 m^2/g, then fall back to around 300 m^2/g if treatment continues. Other bentonites reach 280–320 m^2/g and then steadily fall. A swelling-type bentonite undergoing the same treatment rises from 30 m^2/g to 140 m^2/g then slowly falls (165), thus illustrating how unsuitable it is for activation.

Briefly, then, how is acid activation performed and what are its results? The clay is separated from foreign material such as limestone at the mine site and then transported to the activation plant, where it is crushed to convenient size and, when necessary, excess moisture is dried off. The granulated clay is then slurried with a predetermined proportion of water plus acid, usually HCl or H_2SO_4. The agitated slurry is then heated near its boiling point for a few hours to achieve the desired quality of product from that particular bentonite. Experience and sophisticated testing contribute to the effectiveness of the process regime. Next follows a washing of the clay held in a filter until the appropriate residual acid is reached, then follow drying, grinding, sizing and packing. The proportion of acid used and the duration of the extraction are important factors in the success of the process. Where an increased degree of extraction is necessary, this adds to the chemical and energy costs, increases cycle time and reduces yield of the finished product. Sizing to a particular distribution of particle sizes may also reduce yield and contribute to the finished cost. Nevertheless, the activated clays are so much more effective for many purposes than the neutral ones that many bleaching and purifying steps are rendered economical, practical and convenient by their use.

The important physical and chemical changes brought about by activation are seen as taking place in a distinct sequence.

1. Aluminum, magnesium and iron cations are leached by acid from the octahedral structure at the center of the triple layers. Gaps are created in the crystalline structure, confirmed by X-rays (165), and there is a large increase in internal surface area.
2. The liberated more acidic cations (Al^{+3}, Mg^{+2} and Fe^{+2}) now replace the cations Ca^{+2}, Na^{+} and K^{+}. There is now an increase in the concentration of sites of strong surface acidity—not merely total surface acidity. Furthermore, an increase in activity relates particularly to the increase in the number of 50–200 Å pores, and not just pore volume of any sort (166,235). It is suggested that both these features should be present simultaneously for high quality performance. Lastly, it is observed that from the very beginning of acid treatment there is a pronounced falling off of cation exchange capacity (165). As mentioned earlier, the capacity for easy exchange of

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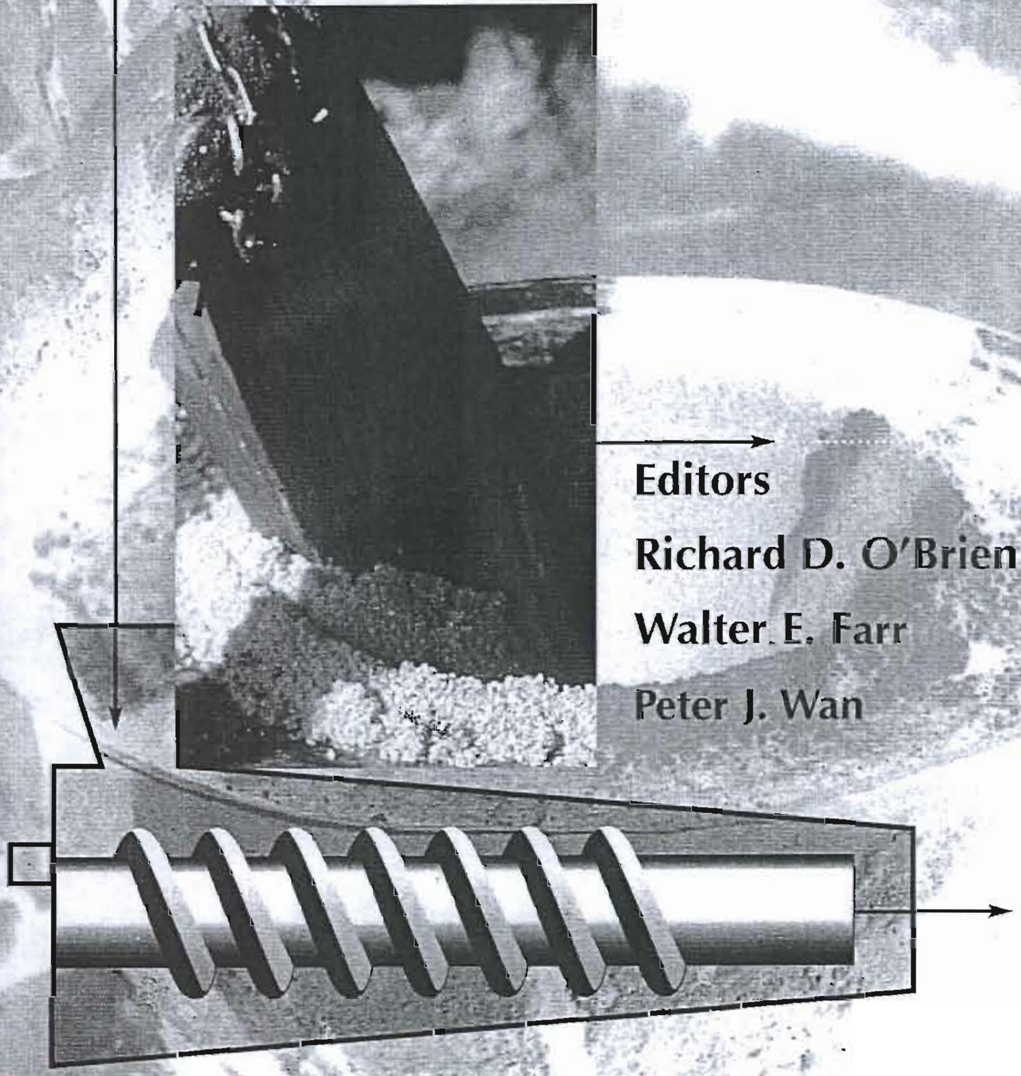
Exhibit 18

Introduction to Fats and Oils Technology

Second Edition



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Chapter 9

Bleaching

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Introduction

Bleaching is an important process used to remove impurities from edible fats and oils. It usually follows neutralization, but it may also follow the degumming process in the case of physical refining. Bleaching is an old process; it is rather complicated and not easily understood. Although degumming and neutralization are strictly chemical processes and deodorization a physical process, bleaching is a combination of the two. An understanding of the bleaching process requires a knowledge of the properties of the bleaching clay as well as the types of impurities present in the fats and oils. This chapter has the following goals: (i) to identify the typical impurities and their sources; (ii) to determine which impurities can be removed with bleaching; (iii) to explain the effects of certain impurities on bleaching earths; (iv) to discuss the most important bleaching parameters such as temperature, time, vacuum, type, and amount of bleaching earth; and (v) to review the possible uses for spent bleaching clay.

Bleaching Earth Structure and Properties

Bleaching earth is made from naturally occurring minerals such as palygorskite, which is also known as attapulgite, sepiolite, bentonite, and other minerals that all belong to the aluminum silicate family. Bleaching earth, often called "fuller's earth," has been known and used for many years (1). The use of fuller's earth for filtration and color improvement of oils was identified and developed by W.B. Albright and H. Eckstein for N.K. Fairbanks & Company, Chicago, IL. Initially, in 1880, they developed a process to bleach cottonseed oil with fuller's earth (2). Bleaching earths consist of natural clays, which have "bleaching activity," and others that become active only after a specific treatment. The first activated bleaching earths were developed by Pfirschinger Mineralwerke, Kitzingen in 1907 and by Erdwerke Kronwinkl, Franz Schmidt & Co. in 1909 (3,4).

An understanding of the activity during the oil treatment with bleaching clay requires a review of the physical and chemical properties of the untreated mineral. First, the bleaching clays must exhibit a certain cation exchange capacity. The other important parameters for natural bleaching clays are a high absorption capacity, a certain porosity, and large surface area. Natural bleaching clays can be slightly acidic to slightly basic. For most of the bentonites, the necessary surface area and porosity have to be created. This is usually accomplished by a treatment with acids.

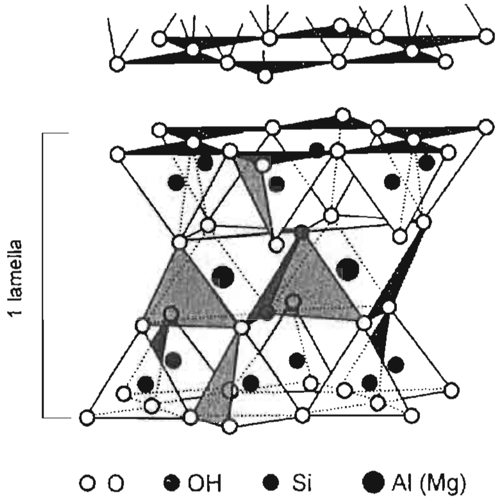

Fig. 9.1. Crystal structure of montmorillonite.

Better activity for certain reactions is obtained by mixing with organic or inorganic acids, or acidification by other methods.

The activation step for montmorillonite, the main component of bentonite, is explained in detail to illustrate the changes in the structure of the lattice and the other reactions during clay treatment.

Activation of Montmorillonite

Montmorillonite is a layer silicate as shown in Figure 9.1 (5). Each layer consists of two silicon layers surrounded by oxygen tetrahedras and an aluminum layer surrounded by oxygen octahedras. Due to the replacement of some of the aluminum ions by Mg^{2+}- and Fe^{2+}-ions, the aluminum silicate layer obtains a negative charge. This negative charge is neutralized by cations, normally alkali or earth-alkali ions, which are in between the negative layers, thus connecting the layers. One crystal contains ~15 layers. Looking at the crystal, it is understandable why montmorillonite has swelling capacity, i.e, the alkali ions, and to a lesser degree the earth-alkali ions, are hydrated, thus expanding the different aluminum silicate layers.

When montmorillonite is treated with an acid such as sulfuric acid, all of the cations located in between the negatively charged aluminum silicate layers are exchanged. With more vigorous treatment, the mineral acid attacks the lattice and dissolves Al-, Fe-, and Mg-ions and destroys the crystal from the edges as shown in Figure 9.2. Without entering into the particulars, it can be concluded that the acid treatment enlarges the surface and pore volume of the montmorillonite to form acid centers. Eventually, with continued treatment, the montmorillonite crystal completely dissolves to form pure silica. Figure 9.3 charts the surface area and activity to show "bleaching activity" with increasing levels of hydrochloric acid (6).

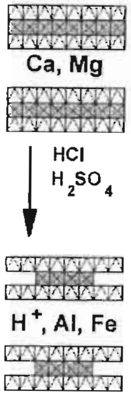

Fig. 9.2. Acid-activated bentonite. The characteristics include exchange of protons, acidic surface, high surface area, and high pore volume.

Obviously, an optimum acid treatment must be determined for the desired activity, depending on the type of acid, its concentration, time, and temperature of the treatment, and last but not least, the crude clay quality.

During activation, the density of the bentonite is reduced. The density reduction is caused by a disorientation of the layers due to the formation of flexible silica tails. This change is illustrated in Figure 9.4.

Another important characteristics of the final product is particle size. It is influenced by the processing steps that follow acid activation. First, the remaining solids from the acid treatment are filtered from the excess acid and the dissolved metal ions.

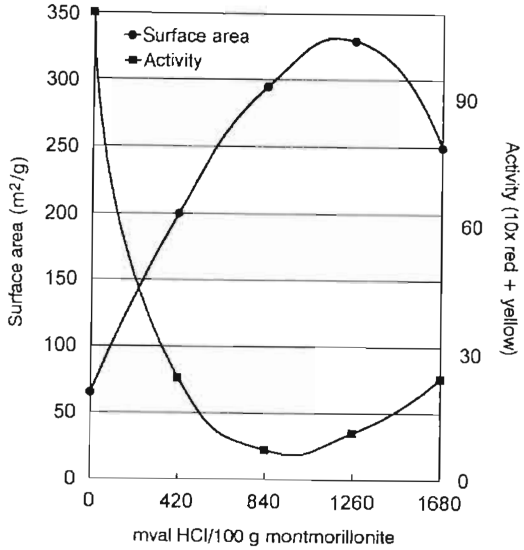

Fig. 9.3. Activation of montmorillonite.

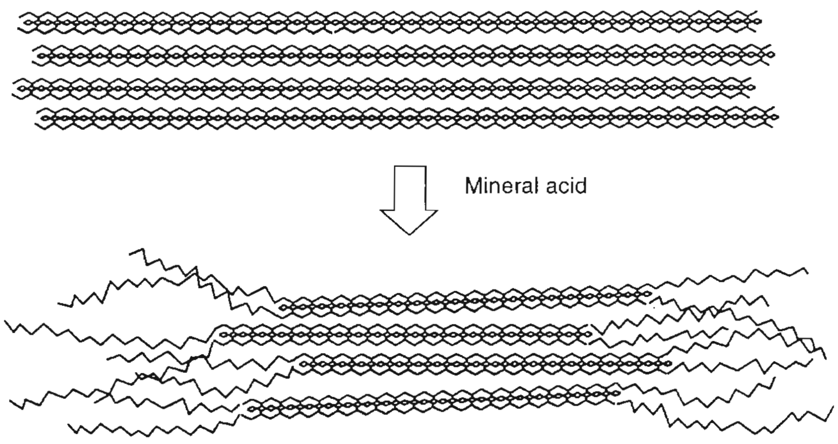

Fig. 9.4. Formation of amorphous silicic acid at the edges of the silicate laminae during acid activation.

The activated clay is then washed to remove the excess acid. The resultant wet clay, which contains ~40% solids, is then dried to evaporate most of the water. The final moisture content depends upon on the type of raw material and the mineral acid used for activation. The moisture content influences the particle size distribution. Optimum filtration properties are obtained with moisture contents ranging from 7 to 15%. Agglomerates of the primary bleaching earth particles are formed during drying; these affect the particle size distribution, which in turn affects filtration and activity. Particle size must be closely controlled because activity increases with particle size reduction; unfortunately, however, filtration decreases as the particle size is reduced (6).

The advantages for an activated bleaching earth include the following: (i) the surface area of the starting material has increased by several hundred percent which results in a high adsorption capacity; (ii) acid activation has provided the clay with some acid centers by formation of silanol groups and by replacing the Ca-ions between the layers with protons and Al-ions, both of which give the clay catalytic properties; (iii) a third important parameter is related to the ion exchange capacity and is strongly related to the ion exchange capacity of the starting clay material.

Activated Bleaching Earth Properties

As discussed previously, the efficiency of a bleaching earth is influenced by the following five characteristics (7): Adsorption capacity, acid properties, catalytic properties, ion exchange capacity, and particle size distribution. On the basis of these characteristics, it is clear that "activated bleaching earth" does much more than simply remove color. The same is partially true for natural bleaching clays, but nature provides some limitations that are eliminated with acid activation. It should also be clear that producers of bleaching earths can optimize a certain product for a specific ble fats and oils that affect flavor, oxidative stability, shelf life quality, eating characteristics, nutrition, and the eye appeal of prepared foods by providing emulsification, lubricity, structure, aeration, moisture barrier, flavor medium, and/or heat transfer (1,2).

Shortening Development

Climate and availability were major influences on the eating habits of our ancestors. Inhabitants of central and northern Europe obtained their edible fats almost exclusively from wild animals and later domesticated animals. Consequently, their foods developed around the use of solid fats such as butter, lard, and tallow. In the more heavily populated areas of Asia, southern Europe, and Africa, where it was impractical to dedicate land to livestock grazing, diets developed with liquid vegetable oils as the major fat source. North American's preference for solid fats was influenced by the early immigrants from northern Europe who adapted large sections of the country to raising domestic animals (3).

Vegetable shortening with all of the physical characteristics of a plastic animal fat was an American invention. It was created by the cotton-raising industry and perfected for soybean oil utilization. Increased cotton production, influenced by Eli Whitney's cotton gin, after the American Civil War made available large quantities of cottonseed oil. Its use as an inexpensive substitute for whale oil used in lamps for illumination disappeared with the development of petroleum industry in 1859. For two decades after the Civil War, cottonseed oil was used in the manufacture of laundry soap or exported to Europe for use in animal feeds or to be mixed with olive oil. Adulteration of olive oil led to tariffs on U.S. cottonseed oil, which discouraged cottonseed oil imports. At home, the hog supply could not keep up with the demand for lard, the edible fat of choice for baking and frying. It had become common practice to mix beef fat or tallow with lard; thus, adulteration with cottonseed oil was a natural step for the use of the inexpensive oil. After public exposure of widespread lard adulteration with cottonseed oil, the U.S. Congress mandated that these mixtures must be identified as "lard compounds." Thereafter, technology developments with vegetable oil processing improved the substitute product to the point that it was superior to the original product in both price and performance. Vegetable oil processors had the foresight at this point to abandon the lard substitute concept to market their products as a food ingredient that has become known as shortening.

Several major technology improvements in oil processing had to take place before substantial quantities of vegetable oils could replace lard as the preferred fat for baking and frying. The first process to be employed concerned hard fat production. It involved a fractionation technique in which stearine was separated by slow cooling followed by straining and draining. This method was attributed to Blondeau in 1761. Initially, cottonseed oil was blended with lard and tallow to produce the adulterated lard; later, however, the lard compounds were formulated with relatively small portions of oleostearine or other hard fats derived from animal fats with the use of a fractionation technique.

Alkali refining procedures were developed in Europe around 1840, but were not employed in the United States until the 1880s. Vegetable oils were alkali refined in open kettles; the foots were separated by gravitation until continuous systems utilizing centrifuges were introduced (4–6). Refining with caustic soda reduced both free fatty acid content and a large portion of the red-yellow color pigment gossypol in cottonseed oils. Caustic-refined cottonseed oils were found acceptable for packing sardines and marginally acceptable for mixing with lard when lard was scarce and expensive. Neutralized cottonseed oil (after caustic refining) retained an acrid flavor and somewhat unpleasant odor, which limited consumer acceptance.

Further color removal from cottonseed oil was necessary to make the oil more acceptable. Initially, bleaching was accomplished by using a palm oil technique that exposed the cottonseed oil to sunlight in large shallow tanks on factory roofs for up to 18 mo. This procedure reduced color but also tied up capital for long periods and damaged the oil flavor and stability. Carbon, the first adsorbent agent used for bleaching, was replaced with bleaching earths. The use of bleaching earths was an American achievement. In 1880, Alexander Winters obtained a U.S. patent for purifying animal and vegetable fats by treatment with pulverized fuller's earth. Six years later, William B. Allbright secured a patent for fuller's earth applied with steam to facilitate removal of oil from the used earth.

Although refining removed free fatty acids and other impurities, and bleaching with fuller's earth solved the color problem, the unpleasant flavor contributed by the vegetable oil portion was so strong that lard substitutes or compounds continued to experience very limited acceptance. The unpleasant flavor and odor limited the amount of bleached cottonseed oil that could be used in lard compounds. Attempts to remove the offensive flavor chemically or mask them with spices or flavors were unsuccessful. Deodorization by blowing live steam through the oil at elevated temperatures was introduced around 1891 and was quickly adopted by most American processors. David Wesson later perfected the deodorization process by exposing the oil to superheated steam in a vacuum to produce a bland-flavored oil with improved oxidative stability. Deodorization enabled the processors to increase the amount of cottonseed oil in lard compounds to ≥80% (7–10) .

Introduction of the catalytic hydrogenation process around 1910 gave the vegetable shortening processor independence from the meat packing industry and initiated a new era for all edible fats and oils, particularly shortening agents. In 1909, the American rights to Normann's British patent for liquid-phase hydrogenation of fatty oils were acquired by the Procter & Gamble Company. Crisco, short for crystallized cottonseed oil, was introduced two years later. The success of the hydrogenated shortening inclined other manufactures to litigation actions, which led to a U.S. Supreme Court decision invalidating Procter & Gamble's exclusive use of the Normann patent and cleared the way for all processors to employ the hydrogenation process. Thereafter, shortening development followed two divergent courses, i.e., all-hydrogenated or compound formulation.

Exhibit 19

Bleaching Considerations For “Organic” Oils

International Conference and Exhibition on Nutraceuticals and Functional Foods
San Diego, CA, Nov. 17-20, 2002

by:

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Abstract

The effect of the bleaching process on the quality of the bleached oil is well documented in the literature. Acid plays a significant role in reaching optimum bleaching activity for chlorophylls and various minor compounds including trace metals, peroxides, soaps, tocopherols and carotenes. Trends toward preserving the natural micronutrients found in various oils and the rising popularity of “organic” labeling practice has raised interest in use of natural bleaching clays. This paper presents an overview of the benefits and issues associated with use of natural bleaching clays. Data will be presented comparing the effects of natural and acid treated bleaching clays on oil quality parameters.

Introduction

The primary goal of the California Organic Foods Act of 1990 (COFA) (1) was to establish standards for growing and processing of organic foods to “optimize the health and productivity of interdependent communities of soil life, plants, animals and people” (2).

The organic foods industry, with ten billion dollars in projected sales by the year 2001 and a growth rate of 20–24% each year over the last decade (3,11), provides a lucrative niche market for any vegetable oil processor that is willing to adhere to the strict guidelines established by National Organic Standards Board.

Organic oils include oils that are produced from plants that have been organically grown and processed in accordance with the California Organic Foods Act of 1990. These oils are naturally processed without chemicals including solvents, caustic agents, mineral acids, and preservatives. Under these processing restrictions these oils are expelled under cold press conditions, water degummed (optional), bleached, and deodorized.

Figure 1 shows the sales distribution of the Organic Oils Market in 1998. The majority of cooking oil sales move through health foods stores (89%), with the balance coming through mass-market grocery stores and other outlets. In a recent comparison between traditional refined and organic refined oils we found that finished oil quality of organic oils was significantly worse than that of traditional (Caustic/Physical Refined) oils (Table 1, Figure 2).

Finished oil quality and stability, regardless of the extraction process, is dependent on the quality of the bleached oil going to the deodorizer as well as the efficiency of the deodorizer.

Efficiency of the bleaching operation is dependent on oil quality, process conditions, bleaching clay properties and desired quality specifications. The effect of oil quality and process conditions on bleaching efficacy, and the role mineral acids play in reaching optimum bleaching activity is well documented (4-6).

Restrictions placed on organic oil processing, however, prohibits the use of acid activated/treated clays. Natural bleaching clays are the only bleaching clay option for processing organic oils.

Objectives

The primary purpose of this paper is to present the various bleaching considerations associated with processing organic oils. To illustrate some of the key points, bleaching activity of six natural bleaching clays (N1-N6) was compared with two acidulated active clays (AC1 and AC2) in treating two organic expelled cold-pressed oils.

Materials and Methods

Oil Sampling:

- Expelled cold pressed organic oil samples were obtained from a commercial source.
- Finished oils were sampled from various local grocery and health food stores. Traditional RBD oils included two name brands and one generic. Traditional oils were sampled from one grocery store while the organic oils were sampled from five different health food stores.

Degumming:

The expelled oil samples were water degummed using 1% water, heated to 75°C, mixed for 30 minutes and then centrifuged for 2 hours at 1200 rpm. Degummed oil was then decanted and stored under nitrogen at 0° C.

Bleaching apparatus:

The reaction apparatus consisted of a 500 ml 3-neck (24/40) distilling flask, two flow- control adapters (24/40), a bevel-seal thermometer adapter (24/40) equipped with a thermometer (0-300 °F), a stir bar and an Electromantle MA heater/magnetic stirrer (Electrothermal, Inc., Gillette, NJ, USA). The apparatus was connected to a nitrogen source and a vacuum pump capable of achieving a 26-28 mmHg vacuum (7).

Clay Analyses:

- X-ray Diffraction: Ground samples were spectroanalyzed using a random powder mount with a Rigaku Miniflex Plus X-Ray Diffractometer (Rigaku, USA Inc., Danvers, Mass., USA). X-rays were generated using a copper target tube with an x-ray generator output of 30 KV 15mA. X-Ray patterns were scanned over range of 3°- 60° 2θ at a rate of 1° 2θ per minute and a sampling step size of 0.03° 2θ.
- Free Moisture: Samples were analyzed on a Cenco Moisture Balance,
- Acidity: pH was determined on a 5% clay/water slurry after 15 minutes slurry time.
- N_2 BET Surface Area and Pore Volume: Samples were analyzed on a Coulter Omnisorp 610.

Oil Analyses:

- Official AOCS Methods were used for measuring Free Fatty Acids, Peroxides, Color and Chlorophyll.
- Tocopherols were measured using an adaptation of the Emmerie-Engel (8) method by Wong et. al. (9).
- Carotenes: Oil dilutions of 1-3 g oil in 25 ml of hexane were measured spectrophotometrically at 442-445 nm.
- Metals: Data was generated by ICP using a P400 Optical Emissions ICP Spectrophotometer (Perkin-Elmer Corporation, Norwalk, Conn. USA).

Results and Discussion

Clay Characteristics:

Bleaching activity of any bleaching clay is dependent on the balance between all of the physical and chemical characteristics of the raw material.

Natural clays (N1-N6) fall into one of two classes of clay minerals: montmorillonite and attapulgite/montmorillonite (A/M) blends
(Figures 3-4).

Natural montmorillonites typically exhibit poor bleaching efficacy and require a mineral acid treatment to achieve acceptable bleaching activity (5). Montmorillonites have filtration problems when used with the modern pressure-leaf filters and, for this reason, are generally ground coarser than A/M blends.

Naturally occurring A/M blends, with the right combination of porosity and surface chemistries, yield a unique mineral combination that exhibits a moderate level of bleaching activity (without the use of mineral acids) and possesses good filtration properties at fine grinds.

Acidity or pH of natural clays is dependent on the nature and concentrations of acid salts and organic materials that occur in the clay deposit. Generally, surface acidity has a positive effect on bleaching; however, the effect is minimal in natural clays when compared to other clay properties such as particle size (grind), porosity and surface area (10).

Table 2 lists the physical and chemical characteristics of the clays used in this study.

Bleaching Activity:

Bleaching, by definition, is the physical and chemical interaction of a sorbent (bleaching clay) with an oil or fat to improve its quality.

Standard bleaching practices apply universally to all vegetable oils (Table 3) regardless of the process. To ensure the highest finished oil quality, the bleached oil going into the deodorizer must meet critical oil quality standards or specifications. For soybean oil, bleached oils need to be free of soaps, bleaching clay particles, or catalyst (if hydrogenated); FFA of less than 0.1%, phosphorus of less than 1 ppm; iron less than 0.1 ppm; and peroxides under 2 mEq/Kg. Color specifications range for red colors from 2.0 to 4.0 while chlorophyll is 30 to 100 ppb (5,6).

Bleaching activity is best determined by measuring the amount of contaminates adsorbed or removed from the oil per amount of bleaching clay used. Bleaching isotherms, which measure contaminant reduction per dosage added, are used in Laboratory settings to determine bleaching activity.

Refineries, however, do not have the time to wait for lab results to make dosage decisions. Refineries tend to track chlorophyll and PVs in the bleached oil to determine bleaching clay dosage. If these two specifications are achieved, specifications for the other contaminants are generally achieved.

Lab bleaches, however, have their place for noting trends and screening products. Lab bleaches were performed on the two degummed organic oils to provide a perspective on the bleaching activity of the various clays listed in Table 2.

Table 4 lists the starting oil quality. Oil 1 was bleached with 0.2%, 0.5% and 0.7% bleaching clay while Oil 2 was bleached at 0.5%. The bleached oil results for the two oils are listed in Table 5. Each of the oils contained 0.2% moisture at the time of bleaching. The benefits of wet bleaching are well documented (5,6).

Although the chlorophyll specifications were achieved by most of the clays, the concentrations of many of the contaminants are still too high. Projections from the isotherm data indicate that 3-6% bleaching clay would be needed to achieve all the bleached oil quality standards for Oil 1.

Figure 5 illustrates the difference in bleaching activity between the natural montmorillonite and A/M blend bleaching clays. The natural A/M blend bleaching clays, overall, demonstrated a higher level of bleaching activity. Furthermore, the two A/M blends (N2 and N6) from the United States exhibited the best overall performance.

In many parameters, the bleaching activity of the natural A/M blend bleaching clays from the USA (N2 and N6) equaled that of the acidulated clays. The acidulated clays demonstrated better bleaching activity than that of the other natural clays.

Summary

- Oil quality standards universally apply to all finished oils.
- An off-the-shelf comparative evaluation of oil quality showed that the quality of organic RBD finished oils was significantly worse than traditional finished oils
- Bleaching plays an important role in reducing detrimental contaminants before deodorization.
- Natural bleaching clays required higher dosages than acidulated clays to reduce contaminants to similar levels.
- Not all natural bleaching clays have the same activity.
- Natural attapulgite/montmorillonite blend bleaching clays demonstrated higher bleaching activity than natural montmorillonite bleaching clays
- Natural attapulgite/montmorillonite blend bleaching clays from the USA performed the best.

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Figure 1

Organic Foods Market Distribution

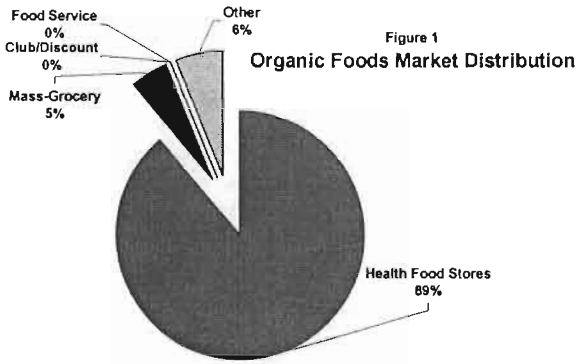
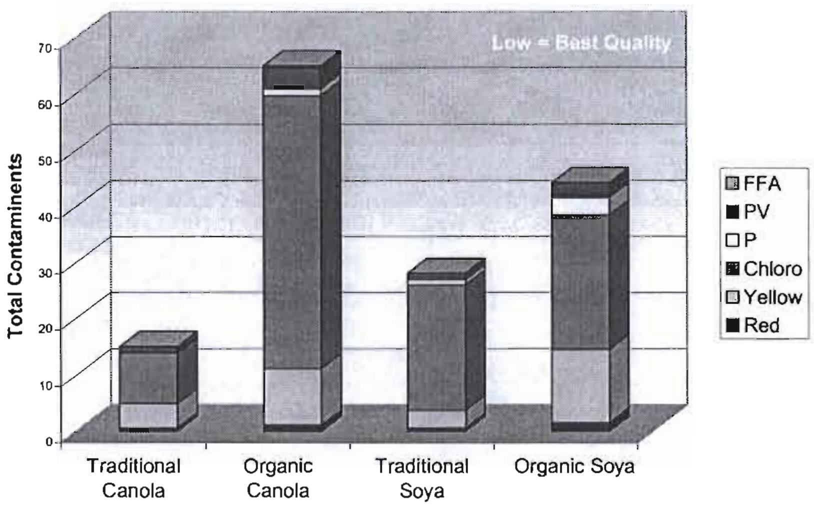


Figure 2

Off-the-Shelf Quality Comparison: Traditional vs Organic



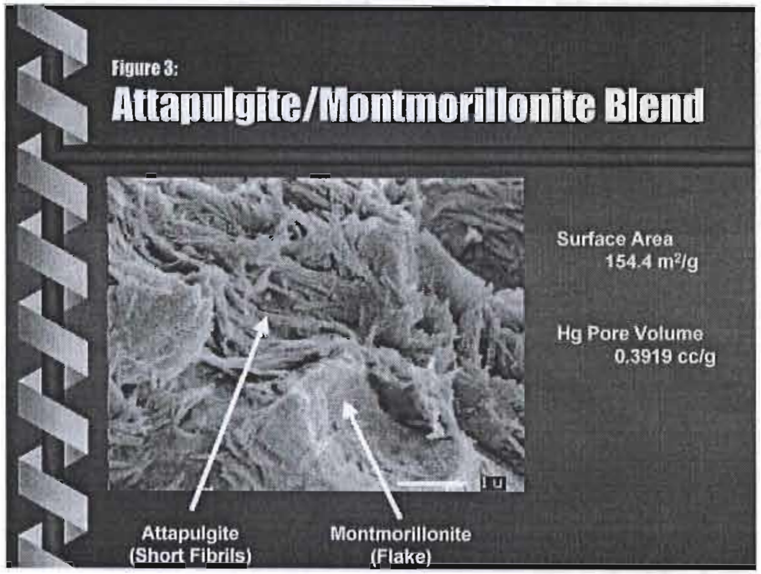


Figure 3:

Attapulgite/Montmorillonite Blend

Surface Area
154.4 m²/g

Hg Pore Volume
0.3919 cc/g

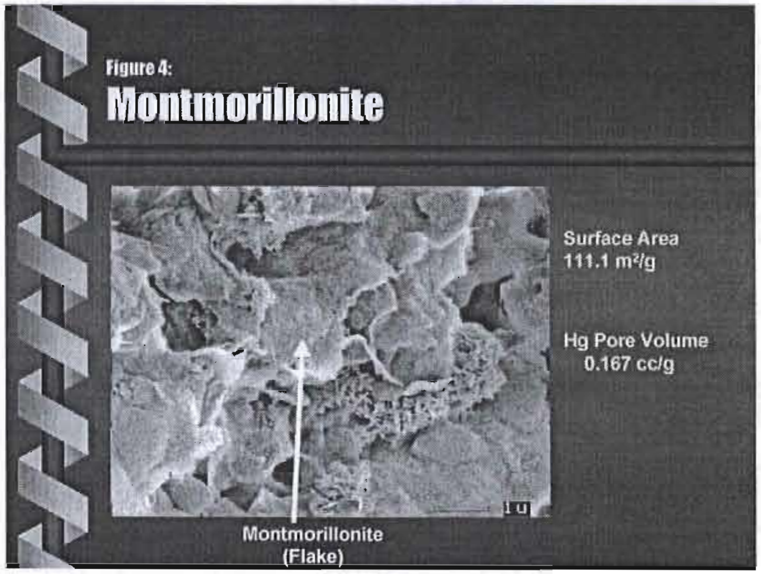


Figure 4:

Montmorillonite

Surface Area
111.1 m²/g

Hg Pore Volume
0.167 cc/g

Figure 5

Overall Average Rank for Natural Clays

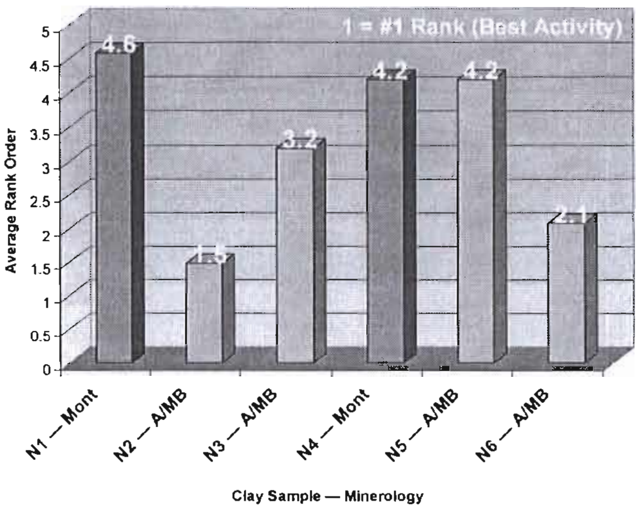


Table 1

Comparison of Organic Oils vs Traditional Oils

Oil Type		Color Red	Yellow	Chlorophyll ppb	Phosphorus ppm	Peroxide Value (mEq/Kg)	FFA %
Canola Oil	Traditional						
	AVG	0.6	4.3	9	0.1	1.0	0.011
	Std Dev	0.0	0.7	3.5	0.1	0.6	0.008
	Organic						
	AVG	1.05	10.1	48.5	1.2	3.8	0.029
	Std Dev	0.3	4.3	33.1	0.6	1.9	0.190
Soybean	Traditional						
	AVG	0.6	3.1	22.3	0.9	1.2	0.005
	Std Dev	0.2	0.7	29.2	0.6	0.5	0.009
	Organic						
	AVG	1.5	13.0	24.0	3.1	2.6	0.039
	Std Dev	0.4	2.8	12.7	3.7	0.7	0.013

Table 2

Bleaching Clay Properties

Bleaching Clay Sample	Clay Source	Mineralogy	Grind % -325 Mesh	pH 5% Slurry	% Free Moisture	N_2 BET Surface Area m2/g	Pore Volume cc/g
N1	Brazil	Montmorillonite	76.0	7.9	7.8	111	0.17
N2	USA	A/M Blend	86.0	6.7	12.4	153	0.37
N3	China	A/M Blend	83.0	9.0	13.5	147	0.32
N4	Indonesia	Montmorillonite	75.0	4.0	9.0	146	0.36
N5	Indonesia	A/M Blend	93.0	8.8	12.4	119	0.31
N6	USA	A/M Blend	92.0	4.1	15.0	151	0.31
A1	USA	A/M Blend	75.0	3.0	11.0	120	0.39
A2	Mexico	Montmorillonite	79.0	3.0	8.7	292	0.51

A/M Blend = Attapulgite/Montmorillonite Natural Occurring Blend

Table 3

General
Bleaching Conditions:

- Dosage:
  - (0.25-1.0%) Low Chlorophyll Oils
  - (0.5-2.0%) High Chlorophyll Oils
- Temperature: 90-120°C
- Contact Time: 20-30 Minutes
- Atmosphere: Vacuum
- Moisture: 0.1 - 0.2% Water

Table 4

Water Degummed
SBO Oil Quality

Bleaching Clay	Red	Yellow	Chlorophyll ppb	Phosphorus ppm	PV mEq/Kg	FFA %
Oil 1	10.2	70	524	24	26.0	0.132
Oil 2	10.6	70	241	53	5.6	0.179

Table 5A

Washed Degummed Cold Pressed
Expelled Soybean Oil Bleached Oil Data: Oil1

Bleaching Clay	Dosage %	Red	Yellow	Chlorophyll ppb	Phosphorus ppm	PV mEq/Kg	FFA %	Carotene ppm	Tocopherol ppm
None	N/A	10.2	70	524	24	26.0	0.132	4393	1332
N1	0.2	9.3	70	287	24	22.5	0.145	3166	1334
(Brazil)	0.5	8.2	70	210	17	19.6	0.141	2602	1332
	0.7	6.7	70	102	14	16.2	0.129	1438	1312
N2	0.2	7.0	70	220	26	19.7	0.153	2115	1246
(USA)	0.5	3.4	70	82	15	13.6	0.142	571	1219
	0.7	2.1	70	55	14	10.7	0.110	251	1154
N3	0.2	9.4	70	406	23	21.0	0.140	3103	1272
(China)	0.5	8.6	70	74	15	16.3	0.135	2259	1206
	0.7	7.8	70	44	14	11.3	0.120	1790	1264
N4	0.2	9.2	70	305	24	20.8	0.146	3007	1269
(Indonesia)	0.5	7.5	70	77	14	15.2	0.135	1647	1162
	0.7	6.0	70	49	18	11.1	0.133	992	1184
N5	0.2	9.6	70	261	24	22.4	0.145	3373	1336
(Indonesia)	0.5	8.9	70	120	19	16.8	0.138	2448	1301
	0.7	8.3	70	60	18	12.7	0.123	1967	1253
N6	0.2	7.3	70	187	20	20.6	0.148	1842	1252
(USA)	0.5	3.6	70	66	17	11.8	0.133	522	1214
	0.7	2.5	70	45	17	8.9	0.119	288	1158
AC 1	0.2	7.1	70	85	24	18.7	0.145	1479	1245
(USA)	0.5	3.1	70	34	18	7.8	0.178	392	1224
	0.7	2.1	70	25	14	3.5	0.150	168	1130
AC2	0.2	7.1	70	96	23	16.6	0.150	1627	1296
(Mexico)	0.5	2.9	70	37	16	5.3	0.155	291	1234
	0.7	1.8	70	26	17	2.4	0.140	131	1187

Bleaching Conditions: 200g Oil, 120°C, 30 min, vacuum

Table 5B

Washed Degummed Cold Pressed
Expelled Soybean Oil Bleached Oil Data: Oil 2

Bleaching Clay	Dosage %	Red	Yellow	Chlorophyll ppb	Phosphorus ppm	PV mEq/Kg	FFA %	Carotene ppm	Tocopherol ppm
None	0	10.6	70	241	53	5.6	0.179	—	—
N1	0.5	8.5	70	67	49	4.3	0.153	—	—
N2	0.5	3.4	70	28	43	1.3	0.135	—	—
N3	0.5	9.4	70	49	46	3.9	0.146	—	—
N4	0.5	8.5	70	50	47	3.4	0.168	—	—
N5	0.5	9.8	70	44	42	3.6	0.159	—	—
N6	0.5	4.7	70	31	46	1.5	0.157	—	—
AC1	0.5	5.0	70	24	42	1.5	0.172	—	—
AC2	0.5	4.6	70	22	40	1.4	0.170	—	—

Bleaching Conditions: 200g Oil, 120°C, 30 min, vacuum

Exhibit 20

MAY - 1 2009

PROCEEDINGS

of the 1999 PORIM International Palm Oil Congress

EMERGING TECHNOLOGIES AND OPPORTUNITIES IN THE NEXT MILLENNIUM

CHEMISTRY AND TECHNOLOGY CONFERENCE

PALM OIL RESEARCH INSTITUTE OF MALAYSIA
Ministry of Primary Industries, Malaysia

Bleaching Factors that Effect Oil Loss

David D Brooks*

ABSTRACT

Refiners often relate oil loss in the bleaching process with oil retained in the spent filter cake. Although FFA levels are more associated with oil loss through the deodoriser, refiners tend to overlook the fact that these levels are the end result of the bleaching process. Starting FFA levels in a crude oil can be adversely affected by bleaching conditions and the acidity of the sorbent used. Small changes in FFA levels can have a great impact on oil loss. Mathematical models show that a FFA rise of 0.1% for a refinery with a production rate of 1000 tonnes per day will result in an annual oil loss of 365 tonnes. This paper reviews the effect oil retention and FFA rise has on oil loss through the bleaching process and how these effects can be controlled.

Various bleaching sorbents from the US, Indonesia, Malaysia and Latin America. were used to treat three palm oils: two from Malaysia (DOBI 2.8, 4.0% FFA and DOBI 2.9, 3.7% FFA) and one from Latin America (DOBI 2.3, 4.12% FFA). Bleached oils were monitored for colour, oil retention and FFA effects. Statistical data shows that the neutral and natural clays lowered or had no effect on FFA while acid activated clays raised FFA. Oil retention for fourteen clays, typically used in palm oil refining, averaged 28% with a 5% standard deviation. Considering these findings, a 0.1% rise in FFA would have over three times greater oil loss than a 5% variation in oil retention (1000 tonnes per day with 0.6% dose, 28% ± 5% oil retention).

INTRODUCTION

In the edible oil refining process, finished oil quality is dependent on the removal of trace metals and various organic impurities known to be detrimental to oil flavour and stability. Production costs are affected by the amount of oil loss in the processes used to remove these impurities, and the cost to operate and maintain the equipment used in the operation. Each stage of the refining process is geared to remove a specific portion of these impurities without causing any additional losses, *i.e.*, elevated FFAs, soaps or oxidisation products. In basic terms, the main objective of each stage is to obtain the best oil quality at the lowest cost.

THE BLEACHING PROCESS

The bleaching operation directly affects the efficiency of the deodorisation and hydrogenation stages. By definition, bleaching is the physical and chemical interaction of a sorbent with an oil or fat to improve its quality. The process refers to the art of removing impurities from a given oil through the addition and subsequent removal of bleaching sorbents.

The bleaching process is generally associated with the selective removal of colourants or pigments from oils by chemisorption. Bleaching, as applied to the palm oil industry, is actually a misnomer. Colour removal alone is unimportant in bleaching palm oil (PORAM 1991) due to the thermal instability of carotenoids under deodorisation temperatures (240°C– 270°C). In a palm oil refinery, the main purpose of the bleaching process is to remove trace metals and various organic impurities that promote oxidation and generate colour-set compounds that are difficult to remove in the deodoriser (Swoboda, 1985; Fraser and Frankl, 1981; Goh, 1985).

OIL LOSS FACTORS

Bleaching Process

The bleaching process can have a sig-

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USA.

nificant effect on oil loss and production costs. Oil loss in the bleaching process results from improper acid pretreat conditions, improper bleaching conditions, level of sorbent needed, and oil retention of the sorbent.

Incoming oil quality directly influences the bleaching operation. Over dosing of acid in the pretreat stage can lead to increase FFA's. Under dosing of acid will result in less efficient removal of phospholipids and increase the demand for higher sorbent dosage.

The literature is filled with papers that cover the effect of bleaching conditions on bleached and finished oil quality (Zschau, 1983; Morgan *et al.*, 1985; Howes *et al.*, 1991; Patterson, 1992). Optimum conditions are listed in *Table 1.* Control of the process variables helps to maximise bleaching efficiency and minimises side reactions that could cause FFA rise or oxidation. FFA rise, due to hydrolysis of triglycerides, is favourable under elevated temperatures. Oxidation tends to occur under elevated temperatures and atmospheric conditions.

TABLE 1. OPTIMAL BLEACHING CONDITIONS

• Contact time	: 20 – 30 min.
• Atmosphere	: Vacuum (27"Hg) or N_2
• Temperature	: 100°C - 120°C
• Moisture	: <1%

Palm oil refiners tend to use neutral or natural bleaching sorbents (pH 4 - 9). Poor quality oils tend to have low DOBI indices and high levels of trace metals, phospholipids and FFA's. Poor quality oils place greater demands on sorbents than good quality oils. In many instances, refiners treat poor quality oils with higher levels of sorbent or resort to looking for a more 'active' sorbent. In many 'active' products, activity is directly associated with increased levels of acidity. Although acid activation of clays is highly beneficial, there are drawbacks to using these 'active' sorbents.

One drawback to using more active clays is that the activation process tends to increase the ability of the sorbent to retain oil. Oil retention is defined as the amount of oil retained in the spent filter cake. Oil loss due to oil retention is directly proportional to the amount of sorbent used. In some oils, the cost of using a more active clay at a lesser dosage may be equal to the cost of using more of a less active clay.

Oil retention can be reported in two different ways: as percentage fatty matter or percentage total organic matter (Patterson, (1992). Fatty matter is usually determined by soxhlet extraction of the spent filter cake with petroleum ether or hexane. The oil and solvent are separated by evaporation and the percentage fatty matter is reported as the weight percent of oil recovered per weight of dry filter cake. The total organic matter is best determined by ashing the spent cake and reported as either the weight percent lost upon ashing per weight of spent filter cake ashed, or as the weight percent lost upon ashing per weight of sorbent added. Oil retention is dependedent on the conditions in which the filter press is 'blown' out.

The term 'blown' out refers to the process of pressurising the press with low pressure steam, air or nitrogen to blow out or release as much of the residual amount of oil contained in the filter bed as possible. Oil retention varies directly with the amount of time the press is blown out. In one of our lab studies, we evaluated oil retention for fourteen sorbents used typically in palm oil applications. Oil retention for these samples ranged from 21% to 39% with an average of 28.0 ± 5.1% Total Organic Matter.

Another drawback to acid activation is the effect the residual acidity has on FFA rise. FFA rise in the oil, through the bleaching process, places more demand on the deodoriser and has a direct impact on the oil loss through the deodoriser.

Deodorisation Process

Although FFA levels are more associated with oil loss through the deodoriser, refiners tend to overlook the fact that these levels are the end result of the bleaching process. Starting FFA levels in a crude oil can be adversely affected by bleaching conditions and the acidity of the sorbent. Small changes in FFA levels can have a great impact on oil loss. Mathematical models show that a FFA rise of 0.1% for a refinery with a production rate of 1000 tonnes per day will result in an annual oil loss of 365 tonnes.

The acidity levels in active sorbents tend to hydrolyse triglycerides more than the neutral or natural sorbents. *Table 2* illustrates the results of a bleaching study involving various clays used to treat three different palm oils of varied quality. In this study each oil was bleached multiple times. The changes in FFA reveal that the sorbents fell into three categories: those that increased FFA (positive change), those that had no effect on FFA and those that lowered FFA (negative change). Data in *Table 3* shows that the acid activated sorbents caused FFA rise. These sorbents tended to have the lowest pH and highest acidity. The natural or neutral clays with high pH and little or no acidity showed no effect or actually lowered FFA.

TABLE 2. BLEACHING EFFECTS of VARIOUS SORBENTS ON FFA: DIFFERENCES BEFORE and AFTER BLEACHING

	Differences before and after bleaching							
Sorbent	A	B	C	D	E	F	G	H
Oil 1	0.11	–0.07	–0.07	–0.06	0.03	0.04	–0.05	–0.10
Oil 2	0.09	–0.04	–0.01	0.00	0.07	0.06	–0.02	–0.04
Oil 3	0.08	–0.02	0.01	–0.01	0.06	0.13	0.03	0.02
Avg.	0.09	–0.04	–0.01	–0.01	0.06	0.08	–0.01	-0.05

Notes:

- Oil 1: Two replicates per sorbent. Conditions: 200g CPO (2.8 DOBI, 3.95 %FFA), Acid Pretreat w/0.075% H_3PO_4 (50% Aq) for 15 minutes w/N_2 at 90°C; Slurry w/1.75% Sorbent for 15 minutes w/N_2 at 90°C; Bleach at 105°C for 30 minutes under 27"Hg vacuum. RBD Colours ranged from 2.6 to 3.1 red (5.25" cell).
- Oil 2: Four replicates per sorbent. Conditions: 200g CPO (2.9 DOBI, 3.72 %FFA), Acid Pretreat w/0.075% H_3PO_4 (50% AQ) for 15 minutes w/N_2 at 90°C; Slurry w/1.5% Sorbent for 15 minutes w/N_2 at 90°C; Bleach at 105°C for 30 minutes under 27"Hg vacuum. RBD Colours ranged from 1.6 to 2.2 red (5.25" cell).
- Oil 3: Four replicates per sorbent. Conditions: 200g CPO (2.3 DOBI, 4.12 %FFA), Acid Pretreat w/0.075% H_3PO_4 (50% AQ) for 15 minutes w/N_2 at 90°C; Slurry w/1.5% Sorbent for 15 minutes w/N_2 at 90°C; Bleach at 105°C for 30 minutes under 27"Hg vacuum. RBD Colours ranged from 2.8 to 3.6 red (5.25" cell).

TABLE 3. COMPARISON OF ACIDITY, pH AND FFA CHANGE

Sorbent	**Classification**	**Acidity mg KOH/g Clay**	**pH**	**Avg. Delta FFA**	**t-Test Results[a]**
A	Acid activated	0.20	2.8	0.09	+
B	Natural	0.00	6.8	–0.03	–
C	Neutral	0.04	5.4	–0.01	NC
D	Natural	0.01	4.4	–0.01	NC
E	Acid activated	0.30	3.3	0.06	+
F	Acid activated	0.03	6.3	0.08	+
G	Natural	0.04	3.6	–0.01	NC
H	Natural	0.00	8.6	–0.05	–

[a] One Column t-Test. 0.05 α, H_0 = difference is zero.
Incorporating delta FFA data across all three oils.

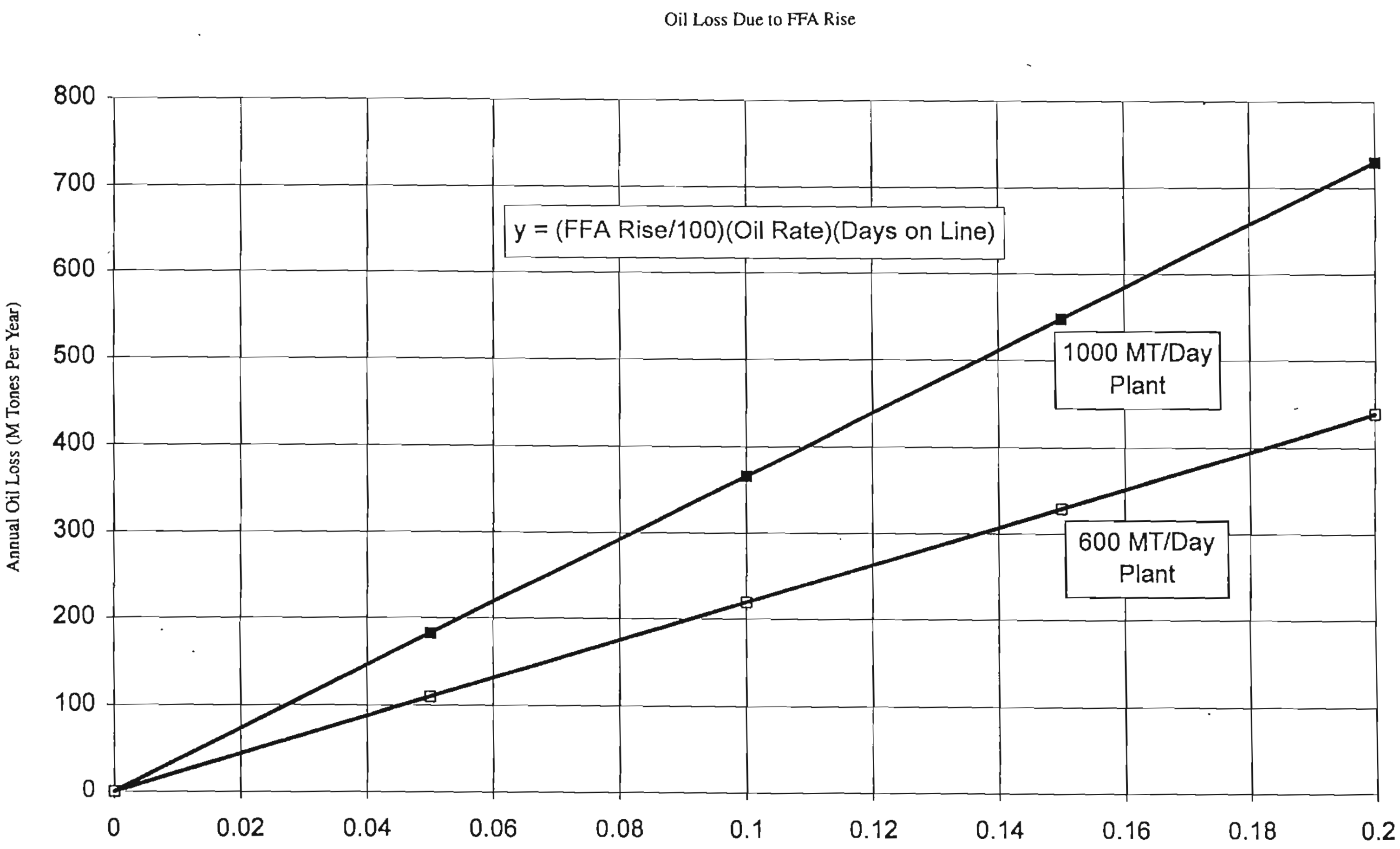

Figure 1. Graphical representation of the effect of changes in FFA on annual oil loss for a large and small scale refinery with a production rate of 1000 and 600 tonnes per day, respectively. A 0.1% change in FFA at a production rate of 1000 tonnes per day would result in an annual oil loss of 365 metric tonnes per year

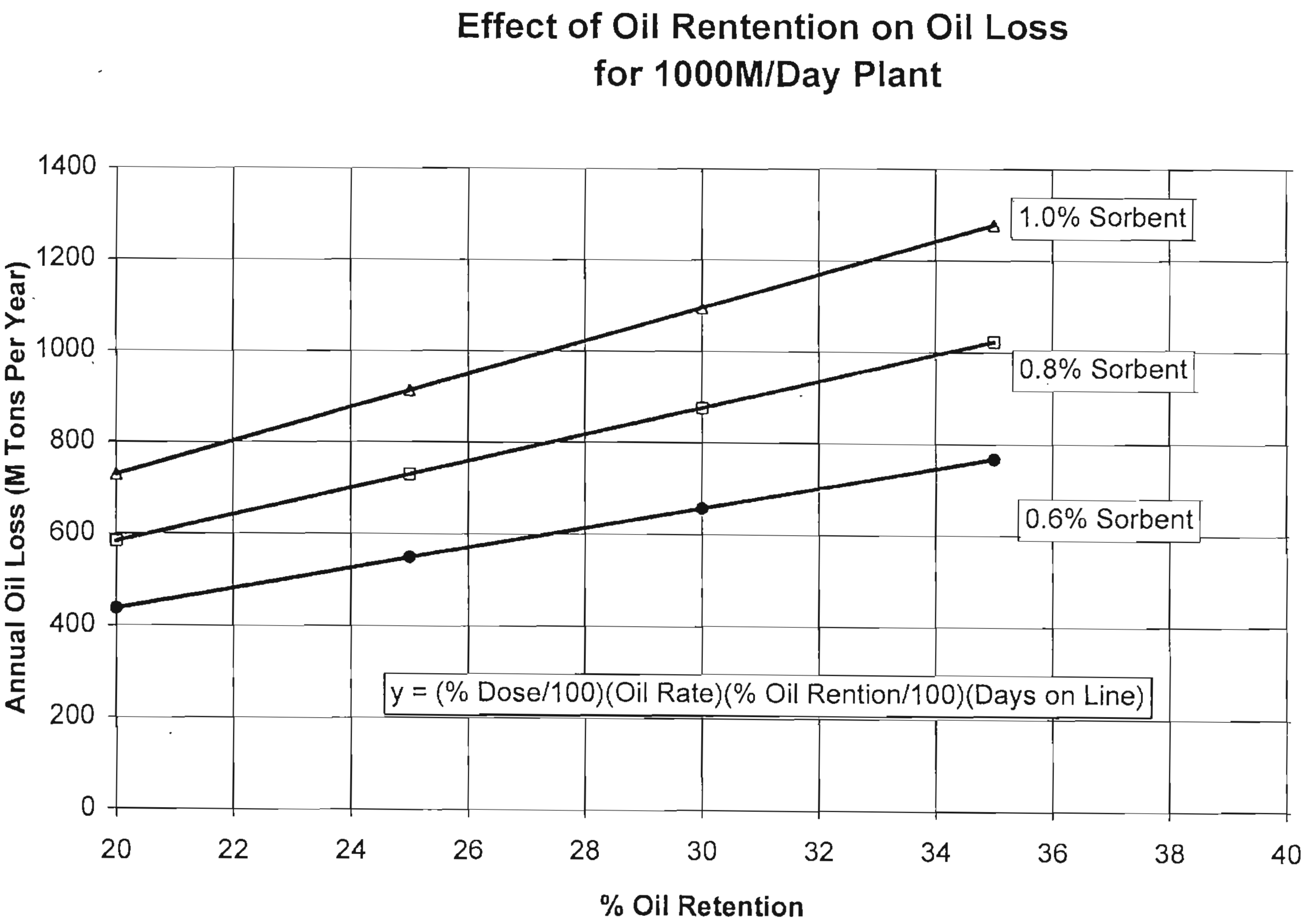

Figure 2. Graphical representation of the effect of changes in oil retention (% total organic matter) on annual oil loss of a refinery with a production rate of 1000 tonnes per day. The average oil retention for 14 sorbents was 28% ± 5%. Oil retention for a refinery with a production rate of 1000 tonne per day at a typical dosage of 0.6% sorbent with 28% oil retention would result in an annual oil loss of 613 tonnes. A 5% change in oil retention would represent a change in 110 tonnes per year

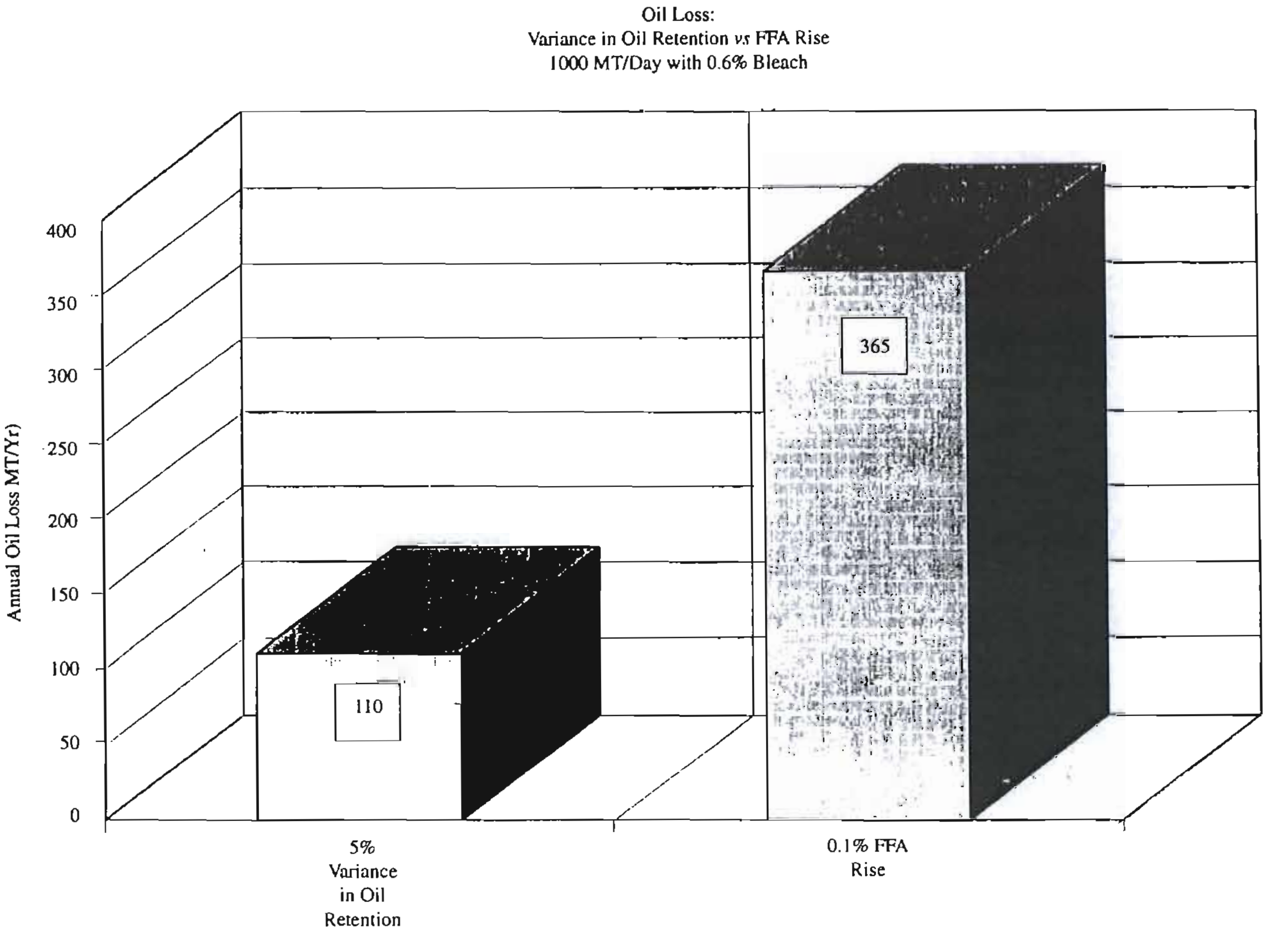

Figure 3. Comparison of the effect FFA rise and oil retention have on annual oil loss

DISCUSSION

Oil loss in the bleaching operation results from oil lost to the filter cake and the oil lost to changes in FFA content. *Figures 1* and *2* graphically illustrate the effect FFA rise and oil retention would have on annual oil loss. As previously mentioned, a 0.1% change in FFA, at a production rate of 1000 tonnes per day, would result in an annual oil loss of 365 tonnes per year. Based on this study, oil retention averaged 28% ± 5%.

A refinery running at 0.6% sorbent with a production rate of 1000 tonne per day with 28% oil retention would have an annual oil loss of 613 tonnes. A variance of 5% in oil retention would represent 110 tonnes per year.

Figure 3 compares the effect FFA rise and oil retention has on annual oil loss. Clearly, changes in FFA have more impact than changes in oil retention. In this illustration, a 0.1% rise in FFA would have over three times greater oil loss than the oil loss due to a 5% variance in oil retention (365 *vs* 110 tonnes).

SUMMARY

The best guideline for controlling oil loss in the bleaching operation is to establish and operate within the optimal bleaching conditions. This maximises the efficiency, prevents the need for higher dosage levels, and minimises oil loss due to oil retention of the sorbent used. Likewise, noting that FFA rise has a greater effect on oil loss than oil retention, refiners need to be cognisant of the potential of sorbents with high acidity (or low pH) to cause FFA rise.

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Exhibit 21

PROCEEDINGS
of the 1999 PORIM International Palm Oil Congress

EMERGING TECHNOLOGIES AND OPPORTUNITIES IN THE NEXT MILLENNIUM

CHEMISTRY AND TECHNOLOGY CONFERENCE

PORIM
PALM OIL RESEARCH INSTITUTE OF MALAYSIA
Ministry of Primary Industries, Malaysia

Relationship between Physical Properties of Bleaching Earths and its Bleaching Efficiency on Palm Oil

Cheah Kien Yoo* and Siew Wai Lin*

ABSTRACT

The physical properties of various types of bleaching earths and their bleaching performance on crude palm oil were evaluated. Adsorption of carotene and chlorophyll were used to measure their bleaching efficiency. The correlation between chlorophyll adsorption and the colour of the deodorised oil was significant. For natural/neutral earths, adsorption of chlorophyll correlated well with the pore volume of the bleaching earth. For acid activated earths, surface acidity played a prominent role in the adsorption of pigment.

INTRODUCTION

Bleaching is an important step in the refining of palm oil. Recently, it has been receiving increased attention because it not only just removes coloured compounds, but also influences the stability of the final oil products. In refining palm oil, the primary function of bleaching earth is to remove trace metals and organic impurities that promote oxidation and generate coloured compounds that are difficult to remove in the deodorizer. Palm oil refiners have a wide choice of adsorbents to use but the main selection criteria remain their cost and performance. At the moment, the criterion of performance is somewhat arbitrary, mainly because of a lack of understanding of the relationship between the physicochemical properties of adsorbents and adsorption of trace constituents in palm oil. This is in spite of numerous attempts to establish the relationship (Morgan *et al.*, 1985; Taylor *et al.*, 1989). This paper will address this issue as part of a continuing effort to ascertain the effect of adsorbent on the final quality of refined palm oil.

MATERIALS AND METHODS

Crude palm oil was obtained from local palm oil mills. Bleaching earths were obtained from their producers through some local refineries. Some of the natural/neutral earths used were not commercial products.

The physical and chemical properties of the earths are listed in *Table 1*. Four of the samples were natural/neutral earths (N1-N4) and the rest acid-activated earths (A1-A5). The pH is that of a 2% (by weight) suspension in deionized water. The surface area was determined by nitrogen adsorption at 77 K with an automated accelerated surface area and porosimetry system, Model ASAP 2010, manufactured by Micromeritics Instrument Corporation (Norcross, GA). Sample weights were 0.2-0.3 g and they were degassed at 673 K prior to the adsorption experiment. The surface areas were determined by the BET equation. The pores were assumed to be slit-shaped, and the pore distribution for all the samples were calculated from the desorption branch of the hysteresis loop by the Kelvin equation. A procedure described by Barrett, Joyner and Halenda - the BJH method - was adopted for calculating the pore size distribution (Webb and Clyde, 1997).

The SCOPA bleach test was used to evaluate bleaching performance using CPO of the quality shown in *Table 2*. Degumming was carried out on 300 g samples of crude oil at 90°C for 10 min with 0.05% (by wt of oil) phosphoric acid. Bleaching was performed with 1% earth at 105°C for 15 min. Nitrogen gas was bubbled through the oil throughout the degumming and bleaching. The bleached oil was filtered under vacuum and then deodourised at 260°C for 20 min at 2-3 torr.

Colour of the deodourised oil was measured in a Lovibond Tintometer with a 5.25-inch cell. Iron was analyzed by atomic ad-

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TABLE 1. PROPERTIES OF BLEACHING EARTHS USED IN THE STUDY

Code of bleaching earth	Type	BET surface area, m²/g	BJH pore volume, cm³/100g	pH (2% suspension)
N1	Bentonite	96	14.2	6.7
N2	Bentonite	139	29.6	7.3
N3	Hormite & smetile smectite	172	34.9	6.5
N4	Attapulgite	141	30.1	7.0
A1	Bentonite	270	38.8	3.7
A2	Bentonite	230	32.8	4.4
A3	Montmorillonite	180	28.7	5.3
A4	Montmorillonite	222	33.5	4.2
A5	Montmorillonite	217	28.1	3.3

TABLE 2. QUALITY OF CRUDE PALM OIL USED IN THE STUDY

FFA, %	2.8
DOBI	2.3
Iron, ppm	5.1
Phosphorus, ppm	7.8
Chlorophyll, ppb	2447
Carotene, ppm	548
PV, meq/kg	1.7
AV	9.7

sorption spectroscopy and chlorophyll was determined by a method described by Tan *et al.* (1994). Determination of peroxide value (PV), anisidine value (AV), free fatty acid content (FFA), carotene content and DOBI were according to PORIM Test Methods (1995).

RESULTS AND DISCUSSION

Quality of bleached and bleached-deodourised oils

Results of the performance tests are given in *Tables 3* and *4*. Peroxides were removed during bleaching and deodourisation. The natural/neutral earths (N1-N4) were less efficient in removing peroxides during bleaching. The influence of the type of earth on the removal of components contributing to AV was less significant. However, most of these components could be removed during deodourisation.

TABLE 3. QUALITY OF BLEACHED OIL

Bleaching Earth	PV (meq/kg)	AV	Carotene (ppm)	Chlorophyll (ppb)
N1	1.3	4.7	529	927
N2	0.3	2.3	467	492
N3	0.3	7.2	412	318
N4	0.5	9.5	516	505
A1	0	5.5	384	193
A2	0.4	9.2	432	333
A3	0.3	6.0	478	395
A4	0	7.7	436	205
A5	0	5.5	390	240

TABLE 4. QUALITY OF BLEACHED AND DEODOURISED OIL

Bleaching Earth	PV (meq/kg)	AV	Lovibond Red	Iron (ppm)
N1	0	1.2	5.7	2.5
N2	0	1.9	2.6	2.2
N3	0	1.9	1.8	1.4
N4	0	3.2	2.1	1.1
A1	0	2.9	1.9	2.4
A2	0	4.0	2.8	2.7
A3	0.1	2.1	2.4	2.4
A4	0	1.9	2.0	0.8
A5	0	1.5	2.2	1.6

Generally, acid activated earths were more effective in removing the colour components. Two of the natural/neutral earths (N1 and N4) had little effect on carotene but were reasonably effective in adsorbing chlorophyll. The most effective earth for removing carotene and chlorophyll was acid activated earth, A1 that had the highest surface area and pore volume.

All except one of the oil samples bleached by natural/neutral earth, N1, had a colour of less than 3 red. In fact oil with the lowest colour was bleached by natural/neutral earth N3.

Iron removal is important for the stability of the finished oil and it occurs during bleaching. The current permissible limit in Codex Alimentarius for Oils and Fats (1996) for iron is 1.5ppm. Table 4 shows that only 3 of the samples had less than 1.5 ppm iron and two of them were bleached by natural/ neutral earths.

Relationship between colour of deodourised oil and bleaching ability of earths

The removal of colour pigments, especially carotene, is a common and simple visual guide used to gauge the overall performance of a bleaching earth. Boki *et al.* (1994) used the adsorption of carotene to gauge the bleaching efficiency of various bleaching earths. However, this may not be a good guide because it has been reported that colour of bleached oil may not predict the colour of the deodourised oil (Brook and Shaked, 1996; Morgan *et al.*, 1985). This was supported by the present study e.g. the carotene contents of N1 and N4 bleached oils were very similar but the deodourised colours differed significantly. This shows that the efficiency of carotene removal is not necessarily correlated with the bleaching ability of the earth. The other colour pigment in oil is chlorophyll. So far, there have not been many studies using chlorophyll adsorption to gauge the performance of bleaching earth on palm oil. *Figures 1* and *2* show the relationship between colour of deodourised oil and the pigment content in the bleached oil. There is a close match between chlorophyll adsorption and the corresponding deodourised colour for all the bleaching earths. This suggests that chlorophyll adsorption may be a better indicator of the bleaching efficiency of bleaching earths.

Relationship between pigment adsorption and physical properties of bleaching earth

In principle, pigment adsorption is related to the physical and chemical properties of the bleaching earth. The most important properties are surface area, pore volume and surface acidity. Nevertheless, Taylor *et al.* (1989) did not find any relationship between pigment adsorption and the individual physicochemical properties of adsorbents used to bleach soybean oil. Instead, they showed that carotene and chlorophyll adsorption can be described by a rather simple model based largely on both surface acidity and pore volume. However, palm oil has a much higher carotene and lower chlorophyll content than most other oils and the applicability of Taylor's model to palm oil has yet to be proven.

Figures 3 - 6 show the relationship between adsorption of pigment (carotene and chlorophyll) and physical properties (total surface area and total pore volume) of the bleaching earths. There was a closer match for chlorophyll (*Figures 4* and *6*) than for carotene adsorption (*Figures 3* and *5*). The best match was between chlorophyll adsorption and pore volume (*Figure 6*). A closer examination showed that the match for natural/ neutral earths (N1-N4) was better than that for acid activated earths. This suggests that surface acidity plays a more prominent role in the acid-activated earths. The role of surface acidity in adsorption of pigment is well documented (Patterson, 1992). Güler and Tunç (1992) reported that adsorption of chlorophyll on an acid activated earth is essentially a chemical process of interaction of the chlorophyll with the Lewis and Brönsted acid sites of the earth. Hence, for an acid activated earth, adsorption of chlorophyll may be more appropriately described by a model similar to that of Taylor *et al.* (1989) i.e. pigment adsorption correlated to pore volume and surface acidity. For natural/neutral earths, the relationships between physical properties and bleaching efficiency (measured by chlorophyll adsorption) were highly significant.

Although the above results showed good correlation between, individually, adsorption of chlorophyll, and total surface area and total pore volume, studies have shown that not all the surface area or pores of bleaching earths are useful for adsorption of pigment. Taylor's model is only valid for pores of 50-200 Å. The pore size distribution of the bleaching earths used are shown in *Figures 7* and *8*. All the natural/neutral earths, except N1, had pores evenly distributed with most of them bigger than 50 Å. N1 had a narrow distribution, with most of the pores smaller than 50

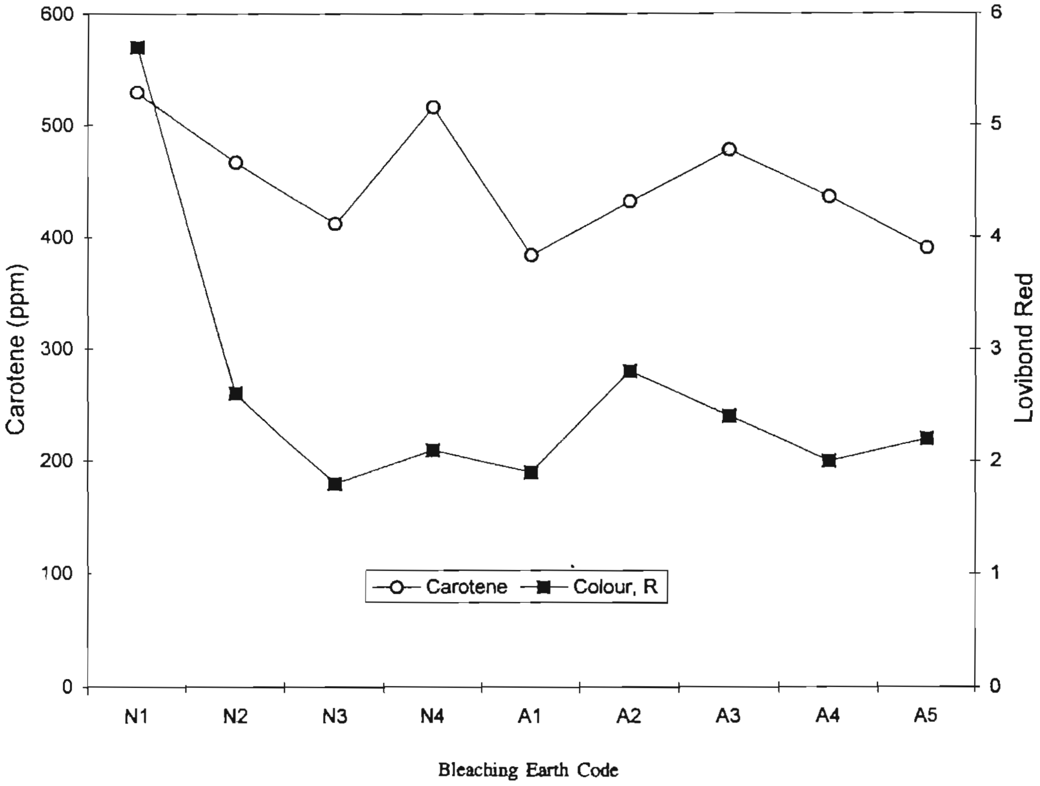

Figure 1. Relationship between colour of deodourised oil and carotene content of bleached oil

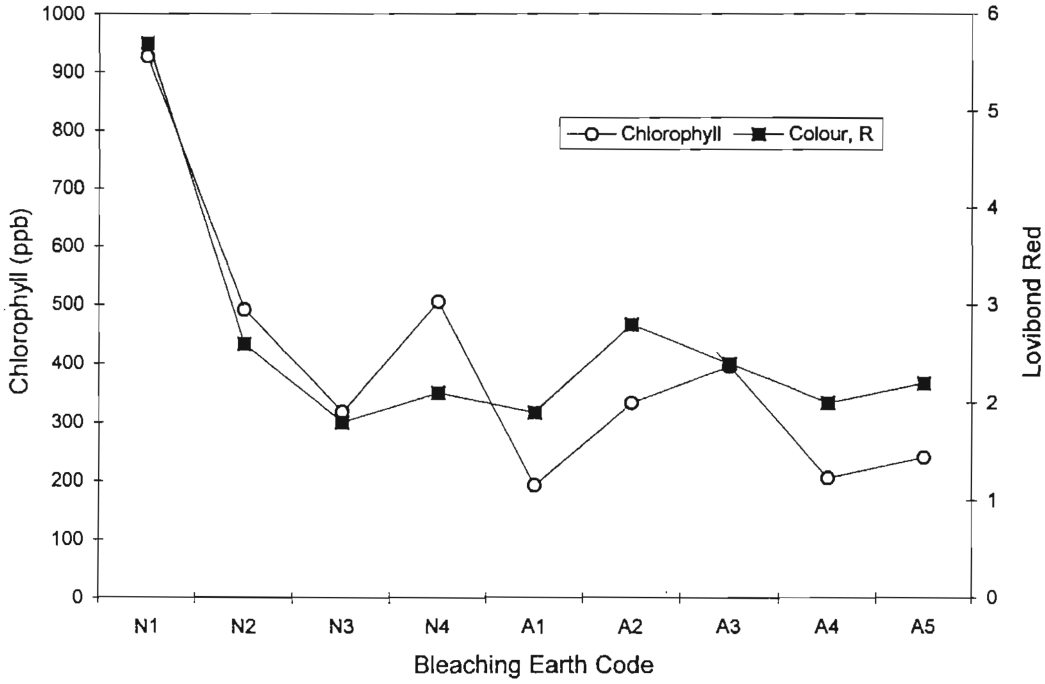

Figure 2. Relationship between colour of deodourised oil and chlorophyll content of bleached oil

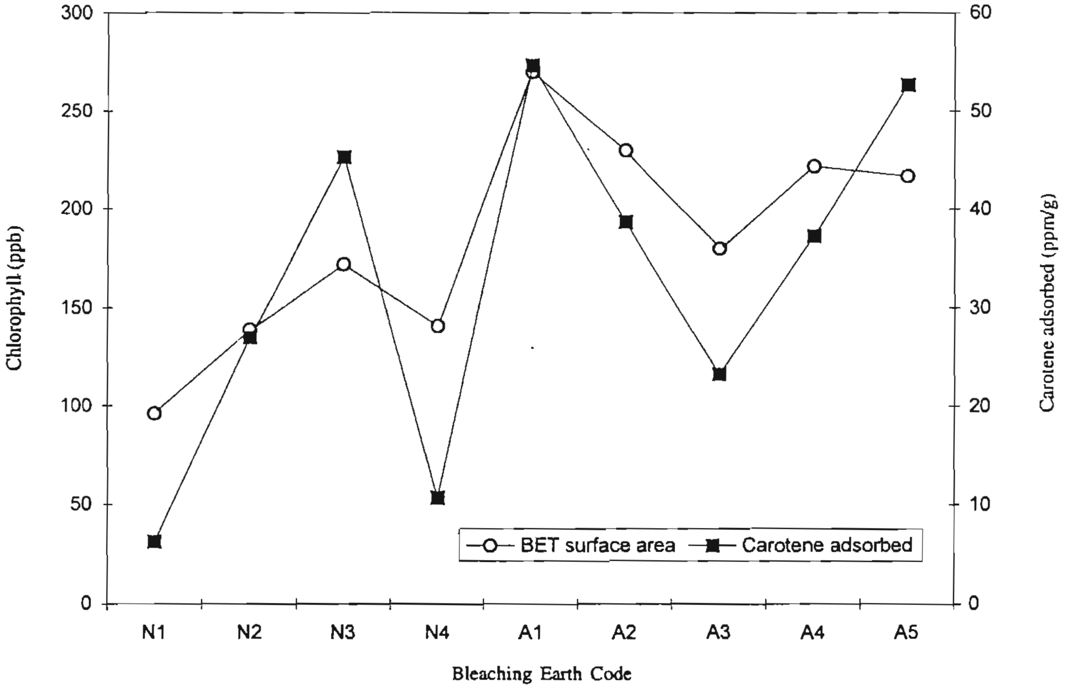

Figure 3. Relationship between carotene adsorption and surface area

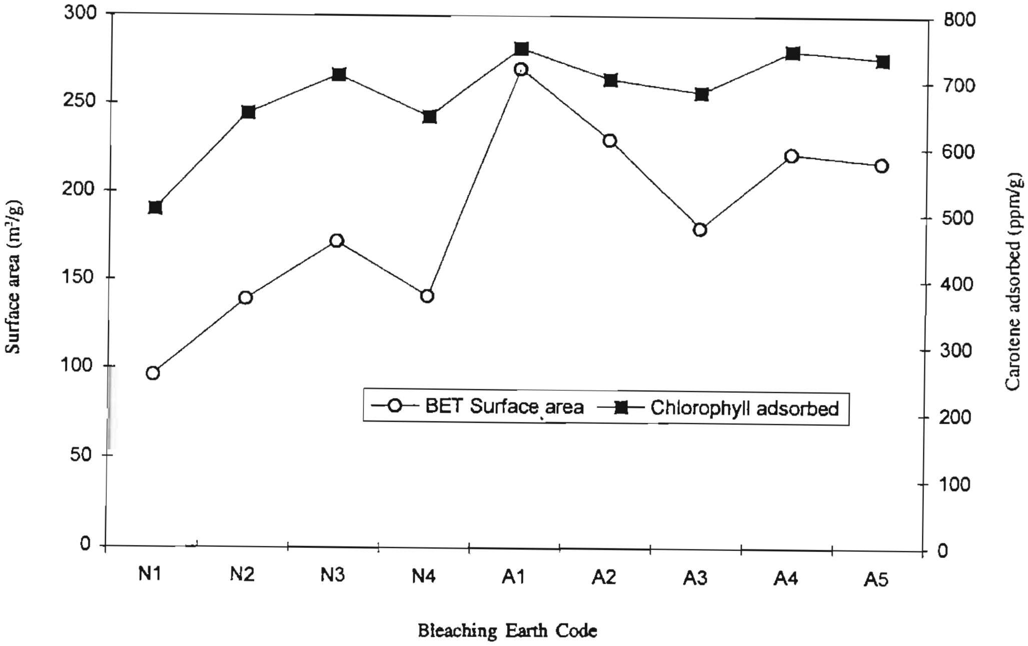

Figure 4. Relationship between chlorophyll adsorption and surface area

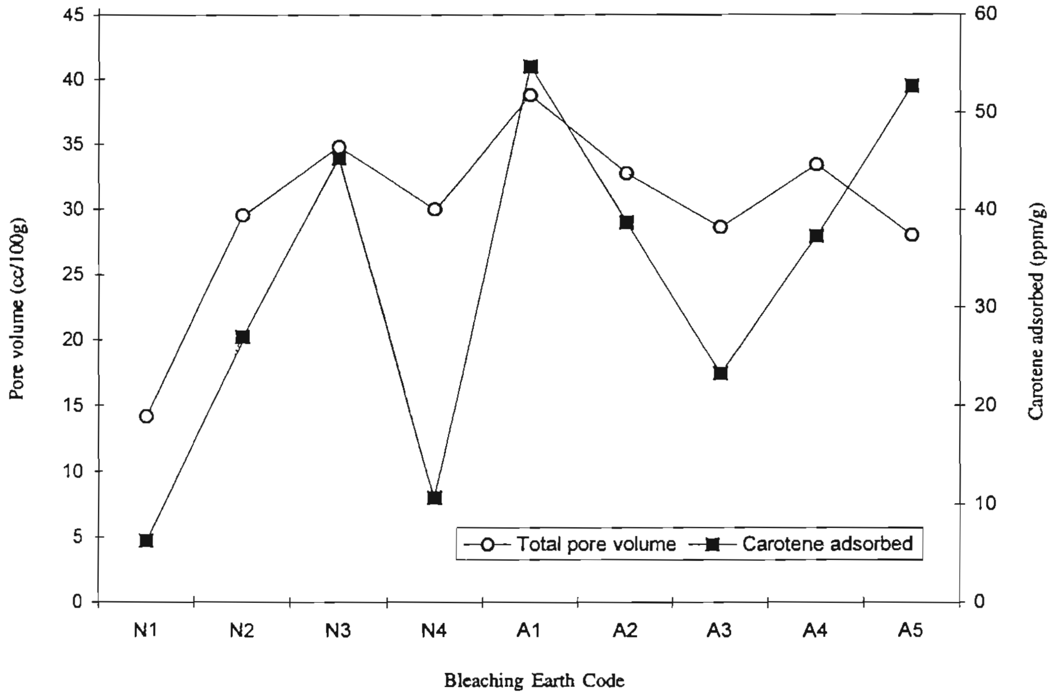

Figure 5. Relationship between carotene adsorption and total pore volume

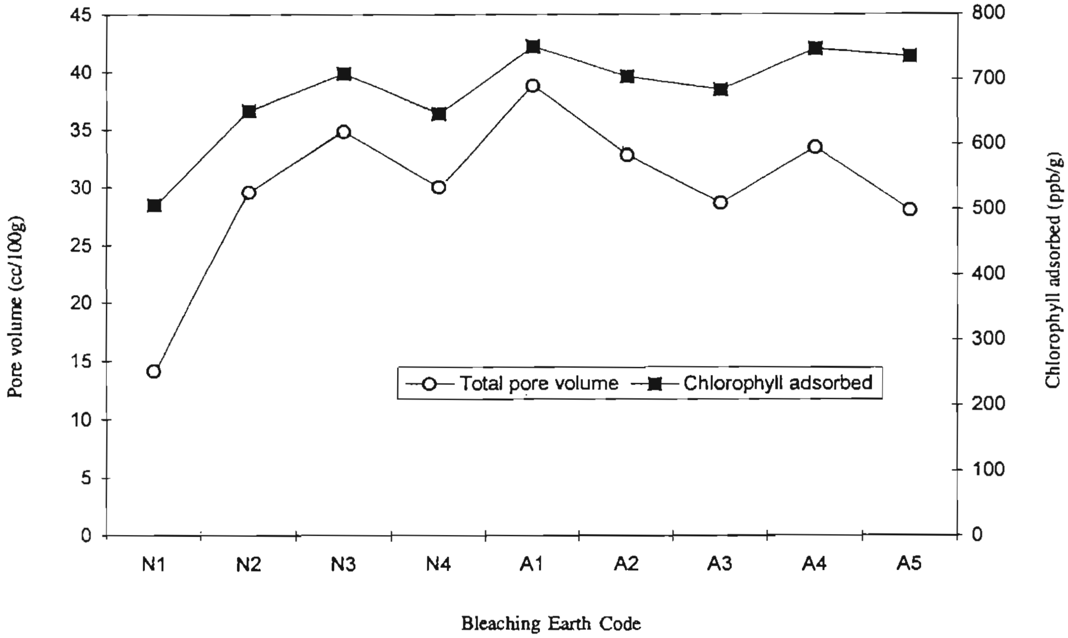

Figure 6. Relationship between chlorophyll adsorption and total pore volume

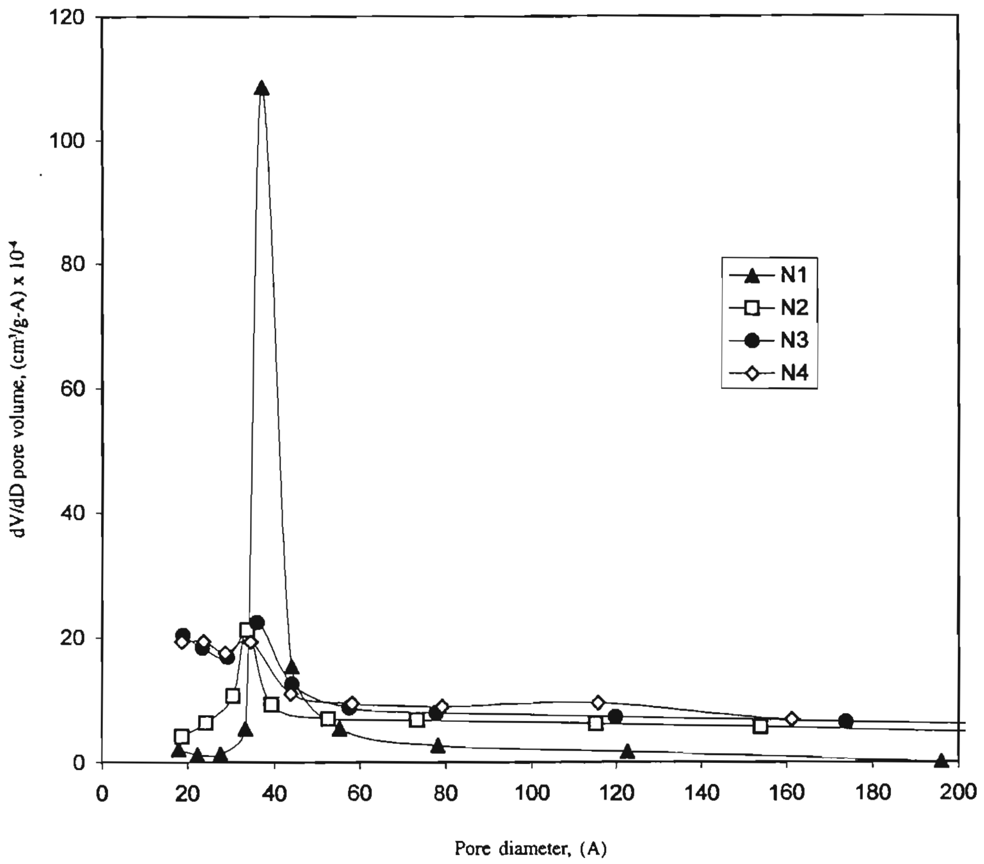

Figure 7. Pore size distribution of natural/neutral bleaching earth

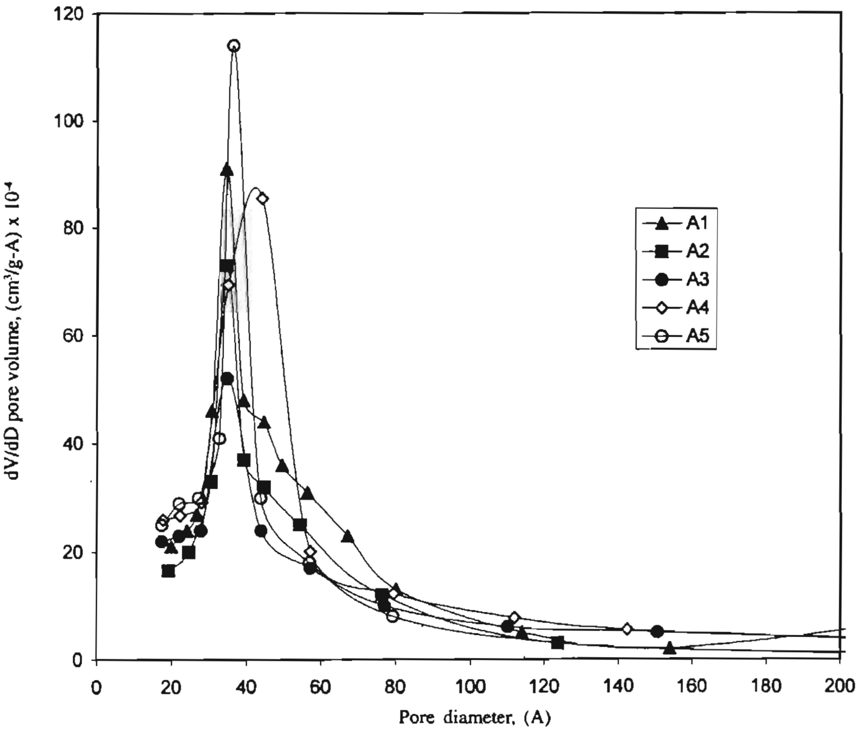

Figure 8. Pore size distribution of acid-activated bleaching earth

Å. All the acid-activated earths had relatively larger percentages (32 - 56%) of their pores smaller than 50 Å. With the present set of earth, no significant correlation was found between pigment adsorption and pore volume of 50-200 Å.

Work is in progress to evaluate more bleaching earths and to quantify the surface acidity of bleaching earth. Taylor et al.'s (1989) model can be tested once these data are available.

CONCLUSION

Bleaching efficiency can be better measured by the adsorption of chlorophyll than of carotene. For natural/neutral earths, adsorption of chlorophyll correlated well with the pore volume of the bleaching earths. For acid activated earths, surface acidity, together with the pore volume, may play a more prominent role in the adsorption of chlorophyll.

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Exhibit 22

Introduction to Fats and Oils Technology

Second Edition

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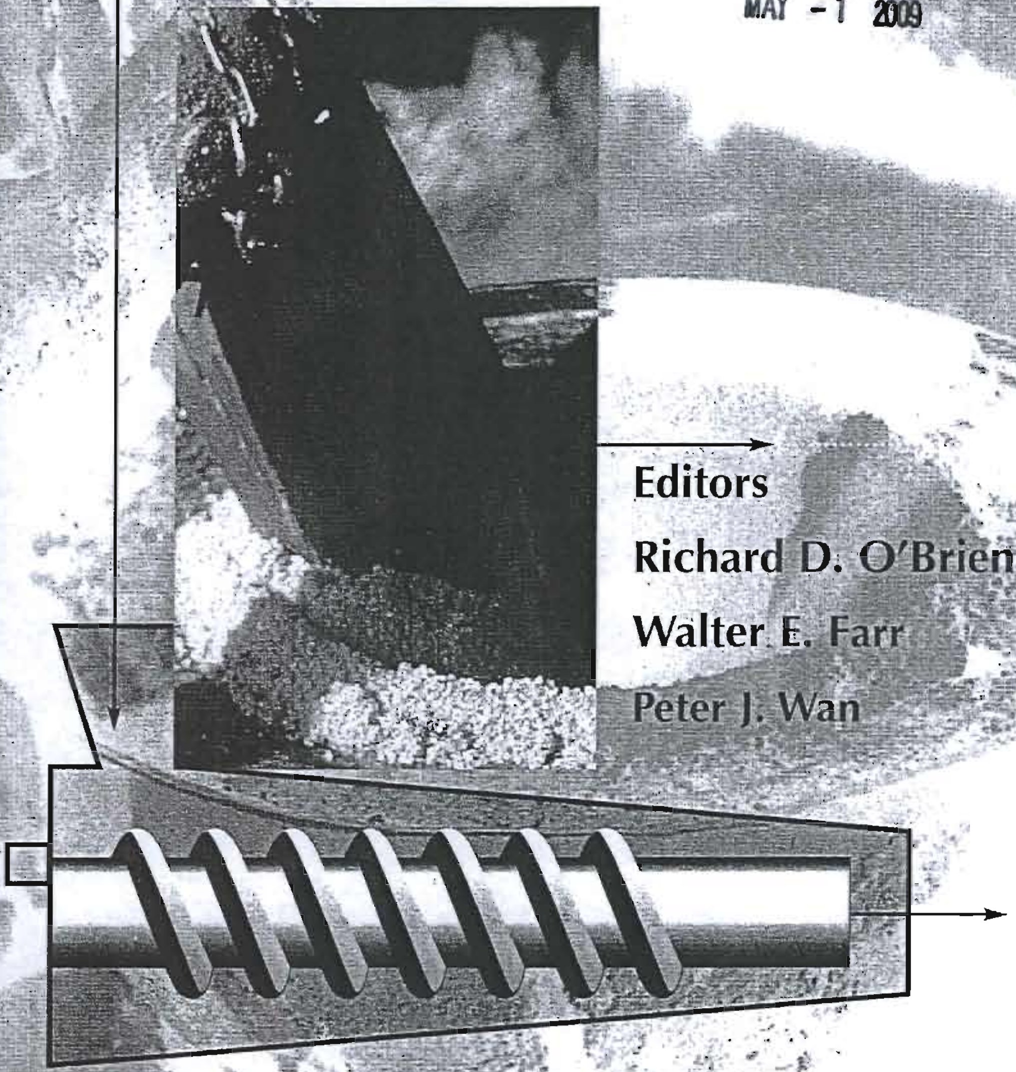

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of the disposal methods must create the least possible harm to humans or to the ecology.

A number of possibilities and processes for utilization of the spent bleaching earth have been evaluated; these include incineration, use in cement production, use in brick manufacture, soil improvement, oil extraction, regeneration, use in bio-gas digesters, use in waste water treatment plants for dentrification, addition to animal feeds, and addition to bitumen products.

Oil Extraction. Deoiling of used bleaching earth salvages a portion of the oil and facilitates dumping of the spent bleaching clay. It has been projected that future regulations may require a reduction of the oil portion of the spent bleaching earth before dumping in a land fill. The following four methods for extracting the oil from the spent bleaching earth were presented at the AOCS World Conference in Amsterdam (19,20): (i) extraction with hexane in the bleaching filter; (ii) extraction with a polar or nonpolar solvent as a separate process; (iii) mixing spent bleaching earth with oil seeds before extraction; and (iv) extraction with hot water in the presence of a surface active agent.

Addition to Animal Feed. Spent bleaching earth, whether used in the edible oil industry or for nonedible oils, contains on the basis of its triglycerides, predominately biologically degradable compounds with a high energy value. Accordingly, there are many possibilities for further utilization. Tests with pigs, poultry, and cattle showed that 3% spent bleaching earth may be added to the feed without any problem (21). Even at these high concentrations, neither vitamin A deficiency nor deficiencies in mineral requirements were observed (22,23). When adding the spent bleach earth to animal feeds, precautions are necessary to avoid contact with atmospheric oxygen to preclude oxidation or even self-ignition.

Use in Biogas Plants. The fine distribution of the fats or oils on the surface of the bleaching earth guarantees a fast decomposition and a high degree of utilization for its biological application. Utilization of spent bleaching earth in biogas facilities is environmentally friendly when certain rules are observed. Essentially, the entire organic content is converted to biogas, thus reducing the increase of CO_2 in the earth's atmosphere as well as improving soils. Soil improvement is also an important consideration. When the sludge of fermented sewage obtained from anaerobic fermentation of fat is spread on agricultural fields, bleaching clay contributes to an improvement of the soil. Bentonite, the natural mineral used to produce bleaching earths, is present in all fertile soils and gives them good water adsorption and water retention capacity. In addition, due to its natural ion exchange capacity, bentonite retains trace elements in the soil, thus improving its fertility. A further benefit was identified by studies in Sweden in the early 1980s, which showed that bleaching clay also helps to reduce the nitrate level in ground water, i.e., surplus organic material helps to reduce the nitrate anion. When used in biogas plants, even small amounts of nickel adsorbed from

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Exhibit 23

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Palm oil-laden spent bleaching clay as a substitute for marine fish oil in the diets of Nile tilapia, *Oreochromis niloticus*

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KEYWORDS

fatty acid • heavy metal • Nile tilapia (*Oreochromis niloticus*) • palm oil • spent bleaching clay

Abstract

A 8-week feeding trial was conducted to determine the effect of substituting fish oil with palm oil-laden spent bleaching clay (SBC), a by-product from crude palm oil (CPO) refining, on growth, feed utilization, fatty acid composition and heavy metal accumulation in the muscle of Nile tilapia, *Oreochromis niloticus*. Four isonitrogenous and isolipidic practical diets were formulated to contain 0, 100, 200 or 300 g kg^{-1} SBC. Growth performance of Nile tilapia was significantly better in fish fed the 100 g kg^{-1} SBC diet compared with fish fed the 0, 200 or 300 g kg^{-1} SBC diet. Growth and feed utilization efficiency of fish fed 200 or 300 g kg^{-1} SBC were similar to fish fed the control diet without added SBC. Whole-body composition, body-organ indices and haematocrit of tilapia were not affected by dietary treatments. Fatty acid compositions in the muscle lipid of Nile tilapia were strongly influenced by dietary treatments with progressively elevated levels of total saturates and n-6 PUFA because of the dietary influence of these fatty acids from residual CPO adsorbed onto SBC. A gradual decrease in total n-3 PUFA concentrations were also observed with the ratio of n-3 to n-6 fatty acids in muscle lipids decreasing from 4.75 to 4.41, 3.23 or 2.37 after 8 weeks on the 0, 100, 200 or 300 g kg^{-1} SBC diet, respectively. The arsenic, cadmium and lead concentrations in the experimental diets increased with increasing dietary levels of SBC but the concentrations of these heavy metals in the whole body and bone of Nile tilapia were not significantly different among fish fed the various diets. The present 8-week study showed that in fishmeal-based diets for Nile tilapia, palm oil-laden SBC can totally replace added fish oil. The use of this presently discarded waste product from palm oil refining in tilapia diets will greatly contribute to reducing the impact of rising feed costs in the culture of tilapia in many tropical countries. Other potential benefits may include acting as a feed binder, removal of mycotoxins in fish feeds as well as adsorbing toxic substances present in the culture water.

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Exhibit 24

CLAYS: ATTAPULGITE AND SEPIOLITE

INTRODUCTION

Just to confuse would-be clay enthusiasts, attapulgite is also known as palygorskite and as fuller's earth in the United States. Sepiolite is sometimes called meerschaum of the famous pipe variety. However, attapulgite and sepiolite are sufficiently similar to form what is termed the hormite group: both are complex magnesium aluminum silicates with an open-channel structure which forms elongate crystals. Attapulgite and sepiolite, as well as bentonite, are closely associated in nature. These clays together with bentonite have some common properties such as a medium to high surface area, good sorptive abilities, and excellent decolorizing, binding, and thickening power. Consequently, the three clays have somewhat overlapping commercial uses and may be regarded as rivals. On the other hand, different crystal structures provide equally important differences, such as the fact that bentonite flocculates in salt water whereas attapulgite is virtually unaffected by electrolytes.

CONSUMPTION

When dispersed in water, needle-shaped attapulgite crystals just 1 μm long and 0.01 μm wide form a random lattice entrapping liquid and provide excellent thickening, suspending, and thixotropic (gelling) properties. Sepiolite also forms bundles of agglomerated needles, which disperse in polar solvents like water to create a randomly intermeshed network of fibers in the solvent. The viscosity is thus raised and various rheological properties can be generated through the control of concentration, agitation, and pH. This characteristic combined with chemical inertness allows sepiolite to be used as a carrier.

In drilling fluids, attapulgite and sepiolite perform similar tasks to bentonite, but are regarded as inferior in most respects. However, being virtually unaffected by electrolytes, attapulgite clays (sometimes called "salt water clays") are particularly effective in salt-saturated environments in which bentonite, hectorite, and other montmorillonites fail to maintain their viscosity (Haden and Schwint, 1967). Examples of such environments include saltwater, gypsum-contaminated water, and drilling fluids containing cement (Sawyer, 1986). Sepiolite is stable at the high temperatures encountered in deep wells or in geothermal areas (Mayhew et al., 1979). Other products utilizing rheological effects include thickeners and suspending agents in non-drip paint, liquid detergents, adhesives, flexographic ink, car polishes, and cosmetics (Figure 65).

Attapulgite is used to a minor extent in oil-bonded foundry sands; its binding characteristics are generally inferior to those of bentonite. Both attapulgite and sepiolite have excellent sorptive properties largely because their extremely porous structure translates to a BET surface area of about 150 m^2/g for attapulgite and 300 m^2/g for sepiolite. In addition, substitution of magnesium and iron for aluminum generates an excess negative charge and a cation exchange capacity of 20 to 50 milliequivalents per 100 g (less than smectite but higher than kaolin). These sorptive properties are utilized in numerous ways including pet litter, animal bedding, tank cleaning, and potting mixes, or as a carrier for fertilizers, pesticides, or hazardous chemicals (liquids can be transported as free-flowing solids). Attapulgite is used to decolorize, deodorize, dehydrate, and/or neutralize various mineral, vegetable, and animal oils. It is also used in the manufacture of NCR (no carbon required) papers: the upper or receiving surface of the copy sheet is coated with attapulgite and the lower or transfer surface of the upper sheet is coated with starch containing minute encapsulated droplets of colorless dyestuff. Breaking the droplets by writing or typewriting releases the dye to penetrate the attapulgite, which catalyzes the conversion to a colored product (Haden and Schwint, 1967).

In animal feed, attapulgite and sepiolite are used as binders for pelletized feeds, carriers of supplement (minerals, vitamins, antibiotics), free-flowing additives for feeds in flour, and lubricants to reduce die friction and improve yield in the pelletization process. They are also reported to increase feed efficiency and improve digestive hygiene. Block sepiolite (meerschaum) may be carved.

GENETIC TYPES

Attapulgite and sepiolite deposits may be formed in:

- ☐ epicontinental and inland seas and lakes as environments of chemical sediments, or by the reconstitution of former clays during diagenesis
- ☐ the open oceans in association with fore-arc basins and ocean rises by hydrothermal alteration of basaltic glass, volcanic sediments, or clays
- ☐ calcareous soils by direct crystallization
- ☐ marine deposits formed by slumping and turbidity currents transporting nearshore materials, and from windblown dust
- ☐ weathering crust of serpentinite and magnesite

In general, this formation in soils, lakes, or shallow seas is associated mainly with a Mediterranean to semi-arid climate which was prevalent in the Late Devonian and Carboniferous and Late Permian to Triassic in the northern hemisphere, and in the Early and Late Eocene, Late Oligocene and Late Neogene, and possibly Late Cretaceous in both hemispheres (Callen, 1984).

Consumption of attapulgite in the United States

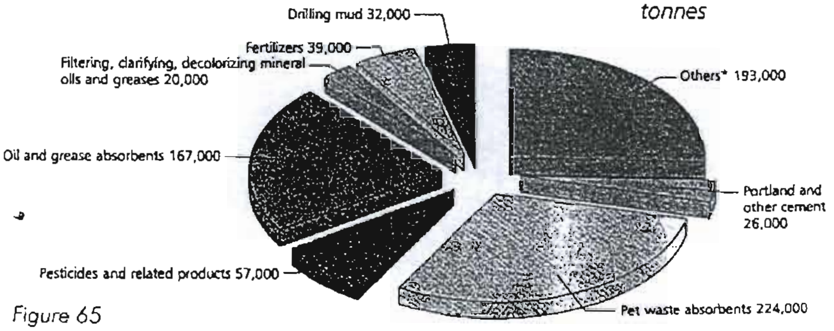


Figure 65

* Includes animal feed, animal oil, gypsum products, absorbents, fillers, extenders, binders, filtering, clarifying, mortar and cement refractories, plastics, roofing tiles, water treatment and filtering, waterproofing and sealing.

Source: USBM (1993)

Table 53 Attapulgite, Sepiolite, Smectite: World Production ('000 tons)

	1990	1991	1992	1993	1994	1995
Algeria	8	5	4	3	5	5
Argentina	2	2	2	2	2	2
Australia (attapulgite)	20	15	15	15	15	15
Germany (unprocessed)	653	708	673	670	498	500
Italy	46	23	28	30	30	30
Mexico	30	41	41	36	214	21
Morocco (smectite)	45	38	38	39	23	23
Pakistan	17	22	22	21	15	13
Senegal (attapulgite)	115	129	112	119	119	120
South Africa (attapulgite)	8	8	8	7	10	8
Spain (attapulgite)	54	73	87	85	85	80
United Kingdom	205	189	189	187	134	130
United States	2,310	2,740	2,410	2,450	2,640	2,640
Total	3,512	3,993	3,630	3,664	3,789	3,586

Source: USGS

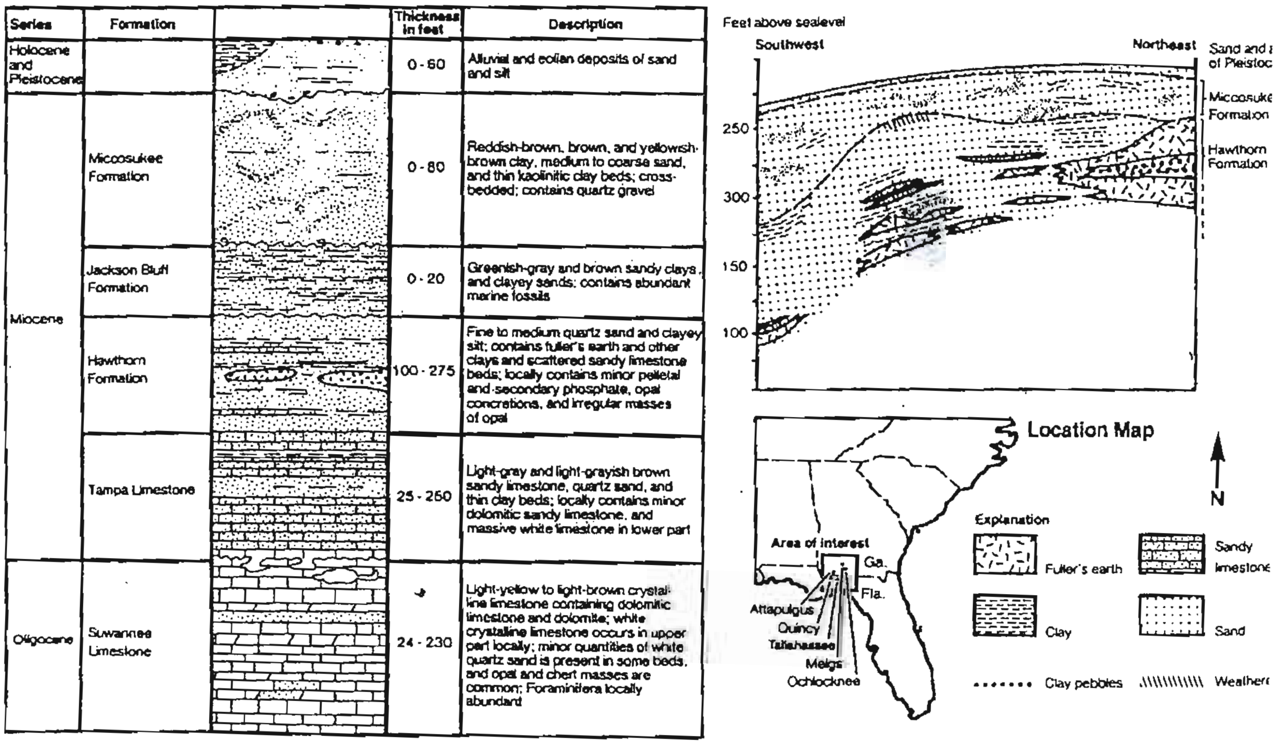
PRODUCTION

UNITED STATES

FLORIDA/GEORGIA

The Meigs-Attapulgus-Quincy district of southwestern Georgia and northern Florida accounts for almost two-thirds of the production of fuller's earth in the United States. The district, in the Coastal Plain physiographic province, is sometimes referred to as the "lime-sink district" because of its abundant solution features. Underlain by Miocene rocks, the fuller's-earth deposits are contained within the Hawthorn Formation — in particular the younger Meigs Member of early middle Miocene age which uncomformably overlies the Dogtown Clay Member of late lower Miocene age. The Hawthorn Formation is present throughout the district and consists of fine- to medium-grained, rounded to subrounded quartz sand intermixed with silt and clay, together with fuller's earth, minor sandy limestone (in part dolomitic), and traces of phosphatic material (see phosphates, page 289). Large lenses of fuller's earth, locally forming continuous beds, extend for more than 80 km from near Meigs, Georgia, to south of Quincy, Florida. Deposits of commercial interest are concentrated at the northern and southern ends of the belt, which are quite different in several respects. Deposits near Meigs and Ochlocknee, Georgia, are 10 to 20 m thick, commonly contain clay-pebble zones, and are usually at or near the top of the Hawthorn Formation. To the south, near Attapulgus, Georgia, and Quincy, Florida, deposits average 2 to 3 m thick, clay pebbles are absent, and there is as much as 24 m of Hawthorn Formation between the deposit and the overlying Miccosukee Formation (Figure 66).

Attapulgite commonly occurs in two distinct forms — short-length palygorskite (<2μm) in the Meigs Member and long-length palygorskite (>10μm) in the Dogtown Member (Merkl, 1989; Heivilin and Murray, 1994). There is also a significant difference in clay mineralogy. In the northern part of the district, attapulgite seldom exceeds 20% of the deposits, whereas in the Attapulgus-Quincy district it constitutes 70 to 80% of some deposits. Sepiolite may form 10% of the deposits in the north, but is virtually nonexistent in the southern deposits. Calcium montmorillonite is often present, as is kaolinite, particularly in the upper, weathered parts of the section. In addition to the mixture of clay minerals, most deposits contain nonclay minerals such as detrital quartz, feldspar, and heavy minerals; authigenic and diagenetic calcite, car-



Series	Formation	Thickness in feet	Description
Holocene and Pleistocene		0 - 60	Alluvial and eolian deposits of sand and silt
Miocene	Miccosukee Formation	0 - 80	Reddish-brown, brown, and yellowish-brown clay, medium to coarse sand, and thin kaolinitic clay beds; cross-bedded; contains quartz gravel
	Jackson Bluff Formation	0 - 20	Greenish-gray and brown sandy clays, and clayey sands; contains abundant marine fossils
	Hawthorn Formation	100 - 275	Fine to medium quartz sand and clayey silt; contains fuller's earth and other clays and scattered sandy limestone beds; locally contains minor pelletal and secondary phosphate, opal concretions, and irregular masses of opal
	Tampa Limestone	25 - 260	Light-gray and light-grayish brown sandy limestone, quartz sand, and thin clay beds; locally contains minor dolomitic sandy limestone, and massive white limestone in lower part
Oligocene	Suwannee Limestone	24 - 230	Light-yellow to light-brown crystalline limestone containing dolomitic limestone and dolomite; white crystalline limestone occurs in upper part locally; minor quantities of white quartz sand is present in some beds, and opal and chert masses are common; Foraminifera locally abundant

Figure 66 Stratigraphic section, cross section, and location map of the Georgia/Florida fuller's earth deposits. Modified from Patterson, 1974.

bonate-fluorapatite, dolomite, and opal; and biogenic material such as shells, fish teeth, and diatoms. The diatom content is high enough in parts of the north to constitute a clayey diatomaceous earth.

Evidence points to the formation of these deposits as sediments in a restricted shallow marine trough which connected the Apalachicola Embayment on the Gulf of Mexico with the Southeast Georgia Embayment on the Atlantic Ocean. The salinity fluctuated while sufficient magnesium was derived from seawater; aluminum and silica came from silicates and dissolved matter carried in solution by streams. Weaver (1984) believes that montmorillonite and kaolinite were probably formed by weathering of attapulgite and sepiolite, whereas Millot (1970) believes the smectite is transformed to attapulgite and sepiolite with small amounts of sepiolite being precipitated. Merkl (1989) states that formation was through the alteration of volcanic detritus, diagenetic alteration of montmorillonite derived from a crystalline upland, and direct crystallization .

The main producers in the area are Engelhard Mineral and Chemicals Corp. near Attapulgus and Quincy (250,000 tons/year attapulgite per plant), Florida; Milwhite at Attapulgus (55,000 to 60,000 tons/year attapulgite), and Oil-Dri Corp. of America near Ochlocknee, Georgia (250,000 tons/year of a mixture of calcium montmorillonite, kaolinite, attapulgite, and diatomite).

NEVADA

Sepiolite along with bentonite, saponite, and hectorite occur in nearly flat-lying beds in the Amargosa Valley, Nevada. Their age is probably Pleistocene, but it may range back to Late Pliocene. Formation is thought to be by the hydrothermal alteration of volcanic ash in much the same way as the bentonite was formed. Accumulation was in a magnesium-rich lake. Variation from saponite to sepiolite resulted from time, temperature, and variations in the concentration of magnesium, calcium, and sodium in hydrothermal waters rising through the dolomitic rocks that underlie most of the area (Mayhew et al., 1979; Odom, 1992). See "bentonite" section.

SPAIN

Annual production of clays in Spain averages 500,000 tons of sepiolite, 95,000 tons of attapulgite, and 50,000 tons of bentonite. Sepiolite and attapulgite constitute important exports.

The major sepiolite producing area is in the provinces of Madrid and Toledo, central Spain. This area forms part of the Tajo Basin, bordered by the Guadarrama and Gredos Sierras on the north and northwest, the Toledo Mountains on the south, and the Iberian Range on the east, which was formed by fragmentation of the Iberian Massif during the Alpine orogenesis, and subsequently filled with Tertiary lacustrine beds including sepiolite. The Vallecas-Vicalvaro deposit, covering a 6.6 km^2 area northeast of Madrid, is reported to be the world's largest known sepiolite deposit. Sepiolite content ranges from 65 to 95% in two exploitable layers: the upper layer grading laterally to dark chert, and the lower layer grading to smectites. Quartz, illite, feldspar, and carbonates are the major impurities. To the south near the city of Toledo the Yunclillos deposit covers about 3 km^2. As in Vallecas, the deposit comprises two layers: the upper varies in composition containing magnesium-smectites and chert as impurities, whereas the lower bed is more continuous and purer (Galan and Castillo, 1984).

Tolsa SA is the world's largest sepiolite producer, with open-pit mines in the Vicalvaro-Yunclillos region. The company has a 600,000 tons/year grinding plant in Madrid, which produces a number of grades of sepiolite used for pet litter (65%), animal feed (25%), and special grades all derived from a high-grade sepiolite (95%+) for value-added technical and industrial products (15%). The sepiolite for this latter use is extracted selectively from a particular seam in the deposit and is produced for use as a catalyst carrier, elastomer filler, and fluidizer of powders. Myta, a subsidiary of the SAMCA Group, produces about 75,000 tons/year of sepiolite in Orera, Zaragoza, and an additional 25,000 tons/year from a quarry at Maderuelo, Segovia. Sepiolsa quarries sepiolite at Madrid and Guadalajara (Regueiro y González-Barros, 1995).

Attapulgite producing areas include the provinces of Caceres in west central Spain, close to the Portuguese border, and Cadiz in the south. Production is dominated by Tolsa SA and Myta (Russell, 1991). Of commercial importance near Lebrija, Sevilla, in the Cadiz area is a sequence consisting of Upper Miocene marine bluish-gray marly clay, overlain by a Pliocene marine sand, and then a continental Pliocene limestone, marl, and clay. These continental rocks contain various amounts of specialty clays. At the base is a marly calcareous bed containing 40 to 80% calcite, 10% quartz, and minor sepiolite and attapulgite; and a rock termed "Tierra del Vino" (after its use to clarify wine), comprising equal proportions of calcite and sepiolite with minor smectite, attapulgite, and quartz. The attapulgite and illite content increases upwards at the expense of sepiolite. The culmination is a 15-m-thick "Palygorskite Bed" consisting of alternating clay, marl, and limestone. The attapulgite content of the clay and marl is 35 to 75%, and reserves are estimated at 9 million tons. The deposits are thought to have formed when sediments were deposited in brackish lake waters. An arid climate and tectonic stability favored the formation of sepiolite, and then significant weathering produced detrital illite, which was transformed to attapulgite in a changing environment that also allowed attapulgite to precipitate directly (Galan and Ferrero, 1982).

ELSEWHERE

Sepiolite and attapulgite are mined in the Provinces of Eskisehir and Kutahya in Turkey from deposits formed by the alteration of magnesite nodules in Pliocene conglomerates. The sepiolite may be white or contain as much as 3% organic carbon. Some is in the sodium-rich form of loughlinite. In Ukraine, attapulgite is exploited in the Cherkassy District near Kiev. In Australia, Mallina Holdings Ltd. produces some 30,000 tons/year of attapulgite at Lake Nerramyne, some 160 km northeast of Geraldton, Western Australia. Around Thabazimbi in northwestern Transvaal, South Africa, Kimony (Pty) Ltd. is mining attapulgite for cat litter and absorbents (Clarke, 1985). Attapulgite is also mined by Ashapura Minechem Pvt Ltd. in the Bhaumagar District of Gujarat State, India.

EXPLOITATION

Production is by open pit with stripping by scrapers, draglines, or bulldozers and extraction by shovels, backhoes, small draglines, or front-end loaders. For example, attapulgite extraction in the Meigs-Attapulgus-Quincy district of southwestern Georgia and northern Florida uses draglines (Clarke, 1985). Processing simply involves crushing, drying, classification, and pulverization. More sophisticated processing may include extrusion, the addition of 1 to 2% MgO to improve viscosity characteristics for drilling muds, heating to yield a low-volatile material or LVM clay with improved sorbent properties, or ultra-fine pulverization to enhance suspension properties for pharmaceuticals (Heivilin and Murray, 1994). In Spain, the clay is sun dried at the mine to reduce the moisture content from about 45% to 32%, and then dried at the plant down to a 12% moisture content.

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CLAYS: COMMON CLAY AND SHALE

INTRODUCTION

Miscellaneous or common clays, together with shale and other fine-grained rocks, receive far less attention in the literature than their aristocratic relatives. This is understandable because common clays live up to their name; these are widely distributed, easily located, and used in products that lack rigid specifications or elaborate processing. More than 60% of the total clay produced in the United States (approximate 26 million tons/year) is common clay and shale, and this proportion is probably higher in other industrialized countries; in some developing countries, production is essentially all common clay and shale.

CONSUMPTION

Since common clay usually needs to be fired to yield a commercial product, it may be defined as a clay or claylike mass that is plastic enough to be readily molded and that vitrifies below 1,100°C. The three major uses are (1) the manufacture of structural clay products such as building brick, drain tile, and vitrified sewer pipe; (2) as a source of alumina and silica in the manufacture of portland cement; (3) for expansion or "bloating" into light-weight aggregate. Shales may be pulverized and added to a clay mix for firing, or they may be used alone as a cement raw material or for bloating to lightweight aggregate. Unfired uses include fillers in paint, asphalt, and other products. Shale and clay are also used for packing dynamite into blastholes and for plugging depleted oil and gas wells (Murray, 1994).

Structural clays have a wide range of physical properties including plasticity, green strength, dry strength, drying and firing shrinkage, vitrification range, and fired color (see table). Highly plastic clays are known as *fat clays*, whereas nonplastic varieties are *lean clays*. Drying and firing shrink the clay which creates cracking and distortion. Sandy clay or clay with low plasticity tend to have low shrinkage rates but produce a weak, porous body; smectites can cause excessive shrinkage. Temperature range of vitrification is especially important. Vitrification is a process of gradual melting, in which increasing amounts of liquid are produced as the temperature is raised. On cooling, this liquid produces glass, which is the bonding agent in the final product. Clays with long vitrification range are preferred, because kiln temperatures do not have to be so rigidly controlled. The degree of vitrification allowed is governed by the amount of shrinkage and porosity needed in the final product. The color of the final product, which needs to be uniform, is influenced chiefly by iron-bearing minerals in the clay or shale — buff-burning clay ordinarily contains 1-5% Fe_2O_3 and red-burning clay 5% or more (Patterson and Murray, 1983; Murray, 1994).

Chemical composition is the governing factor when clay or shale is used as a component of portland cement. These materials provide alumina and silica, and sometimes iron oxide. They are combined with limestone under close chemical control, and the mix is crushed and ground for kiln feed. A clay or shale pit is a common feature of a cement-manufacturing operation.

Certain clays and shales have the property of expanding, or "bloating", to a cellular mass when rapidly heated to 1,000-1,300°C. Two reactions must take place simultaneously: evolution of a gas, and fusion to a liquid that is viscous enough to trap this gas. The gas may be oxygen, sulfur dioxide, or carbon dioxide, produced by dissociation of nonclay minerals. The liquid is a melt like that which forms when ceramic clays are overfired in a kiln. On sudden cooling, the melt forms a porous slaglike material. This is screened to produce a lightweight concrete aggregate weighing 960 to 1,760 kg/m³. Most of the product goes into concrete blocks. The suitability of a clay or shale for manufacture of aggregate is generally determined by experimentation. The chemical composition may indicate whether the material belongs in the group that may bloat, but only actual tests in the furnace will tell whether it will bloat.

Table 54 **Properties of Common Clays**

Property	Mineral influence
Plasticity: the ability of a material to undergo permanent deformation in any direction without rupture under stress beyond that of elastic yielding;	the type of clay mineral, particle size and shape, content of organic matter and soluble salts, adsorbed ions, and the amount and type of nonclay minerals
Green strength: the ability to maintain shape in the wet or plastic state	the type of clay mineral, particle size and shape, content of organic matter and soluble salts, adsorbed ions, and the amount and type of nonclay minerals
Dry strength: the ability to maintain shape after drying	the proportion of fine particles present, the shape of the individual particles, the degree of hydration of the clay fraction, the method of forming the ware, and the rate and thoroughness of the drying
Drying shrinkage: loss of volume during drying	water content, the character of the clay minerals, and particle size
Firing shrinkage: loss of volume during firing	density of the clay, volatile content, types of crystalline phase changes during firing, dehydration characteristics of the clay minerals
Temperature range of vitrification: range of temperature over which clay or shale converts to glass	clays of illite, smectite, or chlorite have a lower vitrification temperature than kaolinitic clays; calcite and feldspar flux the reaction
Color: uniformity of color	state of oxidation and particle size of the iron minerals, firing temperature, degree of vitrification, proportion of alumina, lime, and magnesia in the clay, composition of kiln gasses

Adapted from Murray, 1994

GENETIC TYPES

Minerals that give clay its characteristic plasticity originate by the weathering of complex aluminosilicates that constitute the most common rockforming minerals. Consequently the surface weathering of almost any hard rock with the exception of pure sandstones and limestones can form a clay (Prentice, 1978). The kind of clay mineral produced depends on the climatic conditions — smectites form in dry conditions (pH >7), illite in somewhat wetter conditions, and kaolinite and vermiculite are very wet conditions (pH <7). Still wetter conditions

Table 55 Use of Common Clay and Shale in the United States (tons)

Ceramics and glass*	136,000
Civil engineering and sealing	177,000
Floor and wall tile	
Ceramic	283,000
Other**	45,100
Heavy clay products	
Brick, extruded	11,400,000
Brick, other	1,620,000
Drain tile and sewer pipe	14,000
Flowerpots	35,800
Flue linings	60,600
Structural Tile	37,100
Other***	710,000
Lightweight aggregates	
Concrete block	2,400,000
Highway surfacing	247,000
Structural concrete	801,000
Miscellaneous****	305,000
Portland and other cements	6,920,000
Refractories	303,000
Others*****	311,000
Total	*25,805,600*

** includes crockery/eartheware, pottery, roofing granules, and abarsives*

*** includes quarry tile and miscellaneous floor and wall tiles*

**** includes roofing tile, sewer pipe, terra cotta, and miscellaneous clay products*

***** includes miscellaneous lightweight aggregates*

****** includes firebrick, blocks and shapes, motar and cement, and miscellaneous refractories*

Data for 1994; Source: USGS

may remove the silica to yield gibbsite (Prentice 1990). Ranging in age from Precambrian to Holocene, common clay occurs in everything from glacial clay, soil, alluvium, and loess to shale, weathered and fresh schist, slate, and argillite. "The most common mineral ..... is one of the members of the mica group, and the dominant one in a given deposit may be illite, sericite, or one of the micas normally occurring in coarser grain sizes, such as muscovite and biotite. In addition to illite, the clay minerals present commonly are kaolinite, smectite, mixed-layer varieties, and chlorite. Some materials in this group actually contain more quartz and other detrital minerals than clay minerals" (Patterson and Murray, 1983; Murray, 1994). For example, brickmaking clays, which are mainly sedimentary, are a combination of clastic, authigentic, and biogenic minerals. Quartz is the main clastic mineral with fine sand or silt-sized grains constituting up to 95% of the bulk of the rock. The second in bulk but the most important constituents for brickmaking are the clay minerals such as illite, kaolinite, and montmorillonite. Authigenic minerals commonly include pyrite and siderite, with biogenic minerals such as hydrocarbons and calcium carbonate. Other minerals develop during the weathering process, for example modified clay minerals like vermiculite, sulfates like calcium sulfate and selenite, and iron hydroxide or limonite (Prentice, 1978).

EXPLORATION AND EXPLOITATION

Resources of common clay and shale are "virtually unlimited" (Ampian, 1980). This seems to be a reasonable statement. Suitable clays occur in soil, glacial till, alluvium, and loess, and as weathering products of such rocks as schist, slate, and argillite. As for shale, it is the most abundant of the sedimentary rocks. In geologic age, deposits range from the Precambrian to the present. It is safe to say that supplies of these materials are available for the indefinite future.

As with other minerals, exploration for deposits requires an understanding of the regional and local geology. Appraisal involves sampling and testing of prepared specimens for ceramic properties, content of silica and alumina, or ability to expand on heating. Potential deposits must also be evaluated in terms of transportation costs for these materials of low unit value. As the economic radius for shipment of common clay and shale is less than 300 km, the industry tends toward many local operations, or, in a large firm, several strategically located pits and associated manufacturing plants.

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MAY - 1 2009 **Exhibit 25**

The
Industrial Minerals
HandyBook
4th edition

A Guide to Markets, Specifications & Prices

by

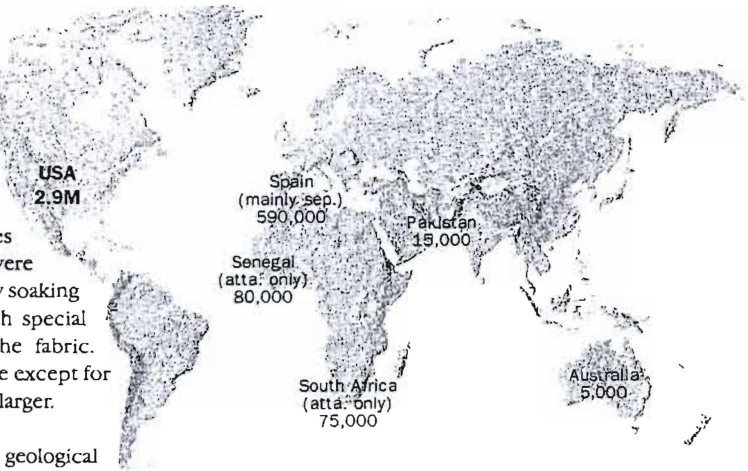
Peter W. Harben

"I keep six honest serving men (they taught me all I knew), their names are:
What and Why and When and How and Where and Who."
Rudyard Kipling (1865–1936)

ATTAPULGITE AND SEPIOLITE

Attapulgite and sepiolite form the hormite group characterized by a complex magnesium aluminum silicate composition, open-channel structure, elongate crystals, and close association in nature. Attapulgite is a hydrated alumino-silicate with an ideal formula where Mg is partially replaced by Al and even Fe. Alternative names are palygorskite (named for the location "in der Paligorischen Distanz" of the second mine on the Popovka River, Urals, former USSR), and fuller's earth (in the United States). The name fuller's earth dates back to the early English wool industry where fullers were textile workers who cleaned newly woven woolen cloth by soaking it in a mixture of water, urine, soapwort, and a clay with special absorbent properties that drew oil and grease from the fabric. Sepiolite is a magnesium silicate that is similar to attapulgite except for an extra silicon tetrahedra which makes the unit cell 50% larger.

Attapulgite & Sepiolite Production (tonnes)



Source: US Geological Survey (2000)

RESOURCES Attapulgite and sepiolite deposits form in various geological environments. Formation in soils, lakes, or shallow seas, is associated with the Mediterranean-type climate prevalent during certain geological times. Formation in inland seas and lakes is as chemical sediments or from the constitution of clays during diagenesis, in open oceans by hydrothermal alteration of basaltic glass, volcanic sediments or clays, or in marine deposits by slumping and turbidity currents transporting near-shore materials. Generation may also be by direct crystallization in calcareous soils or the weathering of serpentinite and magnesite.

Mineral	**Formula**	**Color/Luster**	**SG/*H***	**Remarks**
Attapulgite for Attapulgus, Georgia, USA	$Mg_{1.5}Al_{0.5}Si_4O_{10}(OH)\cdot4(H_2O)$ Magnesium Aluminum Silicate Hydroxide 14.70% MgO 6.2% Al_2O_3 58.43% SiO_2 19.71% H_2O	White, gray; lath-shaped crystals; translucent; dull	2.2 *2–2½*	A.k.a. palygorskite, fuller's earth (in the USA), and less commonly mountain cork or mountain leather
Sepiolite Greek sepion = the bone of the cuttle-fish which is light and porous like the mineral	$Mg_4Si_6O_{15.6}(H_2O)$ Magnesium Silicate Hydroxide 26.26% MgO 58.73% SiO_2 17.61% H_2O	White, grayish, yellowish; fine fibrous crystals, nodular; nearly opaque; earthy to dull	~2 *2–2½*	A.k.a. meerschaum

EXPLOITATION Open pit methods with stripping by scrapers, draglines, or bulldozers and extraction by shovels, backhoes, small draglines, or front-end loaders. Processing is by simple crushing, drying, classification, and pulverization: after processing the product is often divided into gellent or colloidal and sorptive grades. Additional treatment may include extrusion, the addition of 1-2% MgO to improve viscosity (drilling muds), heating to yield a low-volatile (LVM) clay for improved sorbent properties, or ultrafine pulverization to enhance suspension properties (pharmaceuticals).

WORLD CAPACITY Attapulgite 3.0Mt; Sepiolite 800,000-1Mt.

PRODUCTION Attapulgite and sepiolite supply is restricted to a handful of countries with the United States controlling 75% of world production of attapulgite. Spain, and to a much lesser extent Turkey, China, and the United States are the only producers of sepiolite.

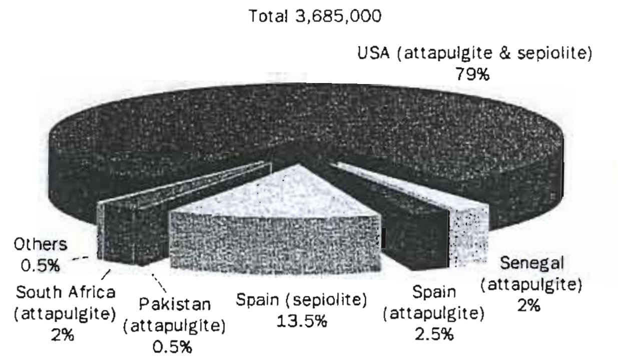
TRADE The leading exporter of attapulgite is the United States (120-150,000 t) with small volumes from Senegal and Australia; Spain (600-650,000 t) is virtually the sole source of sepiolite. Major importers of fuller's earth include Canada and the Netherlands (20,000 t), UK (10-50,000 t), Italy (12,000 t), Germany (10,000 t), and Japan (8-10,000 t). Spain and Turkey export sepiolite.

Harmonized Tariff Schedule 2508.02.0000 (fuller's and decolorizing earths); 3802.90.2000 (activated earths); 2508.40.0050 (other clays).

PROPERTIES AND USES Attapulgite and sepiolite are clays with a chain-type structure (forming needle-shaped crystals) rather than flake-like (bentonite) or plate-like (kaolin) structures.

GELLING PROPERTIES When dispersed, the needle-shaped crystals (1 μm long, 0.01 μm wide) are inert and non-swelling, but form a random lattice entrapping liquid and providing thickening, suspending, and thixotropic (gelling) properties [drilling muds, adhesives, cosmetics, caulks and sealants, minerals greases, liquid detergents, shampoos, flexographic inks, latex paints, epoxy adhesives, polishes, asphalt, acrylic and epoxy sealants and mastics]. The gel formed is a colloidal form of solids suspended in a liquid medium.

Attapulgite & Sepiolite Production



Source: US Geological Survey (2000)

DRILLING MUDS The gelling action of attapulgite and sepiolite is utilized in drilling muds in much the same way as bentonite. However, unlike sodium bentonite, attapulgite and sepiolite do not flocculate with the electrolytes encountered in highly mineralized areas, underground salty water, or sea water (a.k.a. saltwater clay or salt gel) and are stable at high temperatures [saltwater drilling muds, drilling geothermal wells]. Both clays are used in salt-water mud to provide low-shear rate viscosity for lifting cuttings and for barite suspension. When coated with quaternary amine to make them oil-dispersible (amine may be applied to dry clay during grinding or it can be applied to clay dispersed in water), the resulting organophilic attapulgite and sepiolite may be used to provide gel structure in oil muds (although unlike organophilic bentonite, it does not improve the filter cake).

The ability of attapulgite and sepiolite to operate in a salt-saturated media, combined with the high gel strength generated, is utilized in the manufacture of suspension fertilizers for sprinkler systems and irrigation tubes. In the same way, the ability to operate at high temperatures allows organophilic sepiolite to be used as an oil thickener for mineral greases [rheological additive].

COATINGS Attapulgite and sepiolite are used to thicken, disperse, and stabilize various coatings. Sepiolite with cellulosic and other thickeners provides low shear viscosity in latex paints thus improving brush pick-up and preventing syneresis; also used with a surfactant (amine) in solvent based sealants, mastics, and roof coatings. As a co-additive in water-based paint, the clays improve pseudo-plasticity and stability, and micronized grades stabilize emulsion systems. Similarly in solvent-based paints, modified sepiolite provides a balance between leveling and sagging on application. It is claimed that sepiolite "ribbons" are more flexible than attapulgite "needles" and provide a degree of reinforcement.

Sepiolite and attapulgite contribute thixotropic properties to mortars and gypsum, improving application, avoiding sagging, and promoting a smoother finish [rheological additive]. Micronized sepiolite is used as a binder in ceiling panels to improve fire resistance and reduce flammability.

SORPTIVE PROPERTIES Attapulgite and sepiolite have excellent sorptive properties, largely because the extremely porous structure translates to a BET surface area of about 150 m^2/g for attapulgite and 300 m^2/g for sepiolite. In addition, substitution of magnesium and iron for aluminum generates an excess negative charge and a cation exchange capacity of 20 to 50 milliequivalents per 100 g (less than smectite but higher than kaolin) [pet litter, animal feed additive, carrier/diluent for pesticides, desiccants, excipient in pharmaceuticals, floor absorbent, oil spill clean-up material, potting mixes].

PET LITTER Lightweight clays (400-700kg/m^3) used for pet litter include attapulgite and sepiolite, whereas heavyweight clays (800-980kg/m^3) include bentonite. Due to its absorbency, light weight, odor control, and availability, sepiolite dominates the pet litter market in Europe. Along with sodium- and calcium-bentonite, attapulgite is an ingredient of the "clumping" or "scoopable" cat litter that has become so popular since being introduced in the United States at the end of the 1980s. In addition to moisture absorption, features include odor control, lack of dust, light color, and long life; particles are round and microgranular (1-2mm) providing greater comfort for the cat. Sepiolite plus wood particles forms a grit used to line birdcage trays [bird hygiene].

ANIMAL FEED Attapulgite and sepiolite are used as binders for pelletized feeds (reduces friability and dust), carriers of supplement (minerals, vitamins, antibiotics), free-flowing additives for feeds in flour, and lubricants to reduce die friction and improve the yield in the pelletization process. The reduction of moisture and humidity in animal feed handling systems avoids unwanted caking and serious handling problems such as bridging in bins, silos, hoppers and conveyors and facilitates accurate mixing and blending. In addition, some nutritional advantages include a more homogeneous distribution of the micro-ingredients in the feeds, a slower rate of food passage, higher digestibility of nutrients, improved feces consistency, and fewer digestive disorders.

Attapulgite and Sepiolite Trade

Exporters
Australia***
Senegal***
Spain**
USA***

Importers*
Belgium
Canada
France
Germany
Greece
Italy
Japan
Netherlands
Taiwan
UK

** attapulgite & sepiolite;*
*** sepiolite;*
**** attapulgite*

Floor absorbent Attapulgite or sepiolite can absorb more than its own weight in liquid including most oils, water, mixtures of soluble oils and water, grease, acids, inks and paints [garages, service stations, driveways; industrial plants, machine shops, warehouse floors; restaurants, food plants; traction on ice]. In addition to a high liquid absorbing capacity, clays used as floor absorbents need to have good mechanical strength, be chemically inert (will not react with the absorbed liquid), and be nonflammable.

Horticulture Attapulgite keeps soil loose and friable by maintaining a uniform level of moisture and oxygen thus cutting down watering and reduces leaching of water-soluble salts [soil additive]. Sepiolite's large specific area and high water absorption capacity is utilized as an agrochemical carrier for small seed coatings.

Pharmaceuticals Attapulgite can bind to and remove large volumes of bacteria and toxins from the digestive tract and may reduce the fluidity of the stool associated with diarrhea [antidiarrheal ingredient in over-the-counter medicines like *Diar-Aid* and *Kaopectate*].

Desiccant Controlled drying of attapulgite or sepiolite (or bentonite) yields small gray pellets that are a non-hazardous, chemically inert, non-corrosive desiccant, i.e. a hydrating agent attracting and adsorbing moisture from the atmosphere and holding it to itself. The material becomes saturated as moisture is adsorbed or collects on the surface; when heated, the desiccant dries out — or regenerates — and can be used again. Desiccant is used to combat fungus, mildew, odors, rust, discoloration, and product deterioration caused by moisture contamination [electronics, pharmaceuticals, medical diagnostic kits, foodstuffs, footwear, photographic equipment and film, optical goods, batteries, metal and machine parts, museum storage]. Clay is the least expensive of all desiccants and is highly effective below 50°C adsorbing up to 40% of its weight in water vapor at 100% humidity. The desiccant can be successfully regenerated for repeated use at very low temperatures without substantial deterioration or swelling. Activated clay has essentially the same capacity as silica gel at humidity levels of 25-30%, but outperforms it at levels of 20% humidity and below.

Specifications of Commercial Hectorite*

Chemical %	
SiO_2	43.4
Al_2O_3	3.81
Fe_2O_3	1.55
MgO	19
CaO	6.74
Na_2O	2.35
K_2O	0.73
TiO_2	0.27
LiO_2	1.5
Moisture	10% max.
Dry PS	100% -325 mesh
pH	9.5–10.5 (5% dispersion)
Dry brightness	70
Post-fired brightness	90
Viscosity	min. 2000 cps for 5% dispersion (Brookfield LVT @ 60rpm)

** Volclay 353CER (finely ground for use as a binder and plasticizer in ceramic bodies to ease extrusion and increase green strength)*
Source: American Colloid Co.

Bleaching clay The numerous channels or holes (averaging 6Å diameter) of attapulgite or sepiolite are filled with water molecules or hydrated cations that may be driven off by heating to 500°C and so activated to form bleaching earth or clay, a.k.a. activated bleaching earth or activated fuller's earth. Since rehydration is slow, these low volatile material (LVM) clays have enhanced sorptive properties (whereas clays dried at 200°C are known as regular volatile material or RVM).

Bleaching clay derived from attapulgite (or montmorillonite) has excellent oil absorptive and ion exchange capacity plus acid and catalytic properties that are utilized in refining animal and vegetable fats and oils (cottonseed, soybean, sunflower, rapeseed, mustard, peanut, coconut, corn, olive, rice bran, palm, palm-kernel, linseed, castor, jajoba, and canola oils), as well as fatty acids and lubricating oils and waxes. The process consists of (1) degumming, whereby untreated oil at 50-70°C is reacted with 0.1-1% phosphoric acid or less commonly citric acid to remove gums (phospholipids); (2) sodium hydroxide at 95°C may be added to neutralize excess acid and saponify fatty acids in the

Specifications for Commercial Attapulgite

		Grades				
Mineralogy	**(%)**	**0416G**	**1630G**	**2560G**	**050F**	**080F**
Attapulgite (palygorskite)	80–90	4.75mm–1.18mm	1.18mm–0.60mm	0.71mm–0.25mm	85–95% 250μm	85–95% 160μm
Quartz	5–10	MPS 2.36mm	MPS 0.85mm	MPS 0.425mm	MPS 160μm	MPS 35μm
Dolomite	0–10	+4.75mm 3.0% max.	+1.18mm 3.0% max.	+0.71mm 3.0% max.		
Kaolin	0–10	-1.18mm 7.0% max.	-0.60mm 7.0% max	-0.25mm 7.0% max.		

Chemical Analysis (typical %)		**Physical properties**	
SiO_2	58.5	Color	White to light buff/gray
Al_2O_3	11.8	Moisture (as packed)	3.0–8.0% w/w
MgO	5.3	Loose bulk density	0.45–0.65 g/cm³ (450–650 kg/m³)
Fe_2O_3	4	Water absorption	80–120% w/w
CaO	1.6	Oil absorption	70–110% w/w
K_2O	1.8	Surface area (BET)	135–140 m²/g
Other oxides	1.5	Cation exchange capacity	30–40 meq./100g
LOI	15.5	pH (5% suspension)	7.5–9.5

Source: Hudson Resources, Australia

oil; (3) in the bleaching stage, degummed and/or neutralized oil is placed in suspension with bleaching clay which captures the impurities; and (4) the clay combined with impurities are filtered (possibly using a diatomite filter) and thus separated from the bleached oil. During the process, bleaching clay changes the tint of a colored oil by removing color pigments like carotenoids, chlorophyll, and pheophytine without altering the chemical properties of the oil [decolorizing agent]. In a similar fashion, bleaching clay is used to refine animal fats (tallow oil, fish oil, lard oil) and mineral oils (paraffins and waxes, insulating oil, waste lubricating oil, industrial triglycerides and fatty acids used for paints, varnishes, and soaps). In effluent treatment plants, bleaching clays are used to remove impurities, coagulate bacteria, and soften the water through the removal of calcium and magnesium salts.

Sepiolite for Animal Feed

	Binder	Anti-caking agent & carrier
Particle size (mesh ASTM)	<100	50–120
Bulk density (g/l)	545±40	615±30
Moisture (5)	8±2	8±2
Westinghouse oil absorption (%)	–	92±7
Linseed oil absorption (%)	93±5	–
Water retention (%)	150	147
Mohs' hardness	2.0–2.5	2.0–2.5
Cation exchange capacity (meq/100g)	15±5	15±5

Source: Tolsa SA, Spain

MISCELLANEOUS Block sepiolite, known as meerschaum (derived from the Greek ***meer*** meaning sea and ***schaum*** meaning froth for its light weight and color), may be carved into various objects including the famous pipes. In friction materials, micronized sepiolite neutralizes electrostatic charges thus increasing mechanical stability and improving component uniformity and therefore performance and resistance to wear [brake and clutch linings]. Micronized sepiolite is a reinforcing filler in rubber compounds and acts as a processing aid by avoiding deformities during rubber extrusion whilst in the green state.

SPECIFICATIONS General specifications may include granule sizes, dust content, moisture content, and specific sorption requirements. Processed ore may be divided into gellent or colloidal (some with chemical additives) and sorptive grades. ***Drilling muds*** Specifications for gellent grades for drilling muds are covered under API Specification 13A, Specifications for Drilling-Fluid Materials, 1993 (see table) which has similar viscosity specifications as bentonite. Testing involves adding water and mixing slurries of specific concentrations and then measuring viscosity, yield, yield point, filtrate (a measure of wall building properties), and a wet screen analysis according to standard procedures recommended by the API or OCMA. ***Sorptive*** depending on temperature of drying, sorptive grades may be divided into regular, LVM, and RVM. Products in the US range from 4/25 Mesh RVM, 4/25 LVM, to 20/50 RVM and 20/50 ultra hardened granules, as well as micro powders. Covered under Federal Specifications P-A-1056A, Absorbent Material, Oil, and Water (for floors and decks). ***Pet litter*** acceptance as a pet litter depends on absorbency, bulk density, granule size, formation of dust, and odor control. ***Pesticide carriers*** 1-5mm as a regular carrier and <150 µm for application as a dust.

ENVIRONMENT/HEALTH AND SAFETY IARC Monograph Volume 68 published in 1997 (see *Silica and Quartz*) stated that the epidemiological evidence for palygorskite carcinogenicity was inadequate, while carcinogenicity studies with rats indicated that long fibers were carcinogenic — particularly with respect to mesothelioma induction — whereas short fibers were not carcinogenic. Consequently, long palygorskite fibers (>5 µm) were classified as possibly carcinogenic to humans (Group 2B), while short palygorskite fibers (<5 µm) cannot be classified as to their carcinogenicity to humans (Group 3). The same classification was given to sepiolite.

The acicular nature of these clays ("microfibrous morphology") has generated some OS&H concerns. The German Consumer Council identified "microscopic needle-shaped fibers" in cat litter containing attapulgite and sepiolite, although subsequent studies have found them to be harmless. Still the perception remains.

SUBSTITUTES ***Animal feed and supplement*** bentonite, perlite, talc, vermiculite, and zeolites. ***Pet litter*** bentonite, diatomite, gypsum, zeolites. ***Desiccants***: *solid* - clay, silica gel, zeolites, quicklime, calcium sulfate, activated alumina, activated carbon, and lithium chloride salt; *liquid* -

Comparison of Attapulgite, Bentonite, and Kaolin as Thickeners

	Attapulgite	Bentonite	Kaolin
Principal mineral	Attapulgite	Montmorillonite	Kaolinite
Crystal structure	Chain	3-layer sheet	2-layer sheet
Particle shape	Lath-like	Flake	Plate
Particle size	Extremely fine (<0.50µm)	Extremely fine (<0.50µm)	Very fine to medium (0.50–10µm)
Color	Light cream	Variable, gray to white	White
Thickening power	High	High	Medium to low
Effects of salts	Little or none	Flocculates	Flocculates
Method of thickening	Colloidal interaction network	Particle interaction network with swelling	Flocculation at low pH gives medium thickening. At neutral or basic pH its slurries are generally thin and non-thickening

Source: Engelhard Corporation

ATTAPULGITE AND SEPIOLITE

lithium chloride, lithium bromide, calcium chloride, and triethylene glycol solutions. ***Carrier*** bentonite, diatomite, kaolin, peat, pumice, pyrophyllite, talc, vermiculite, and zeolites. ***Thickener and gelling agent*** bentonite, various polymers, and cellulosic thickeners.

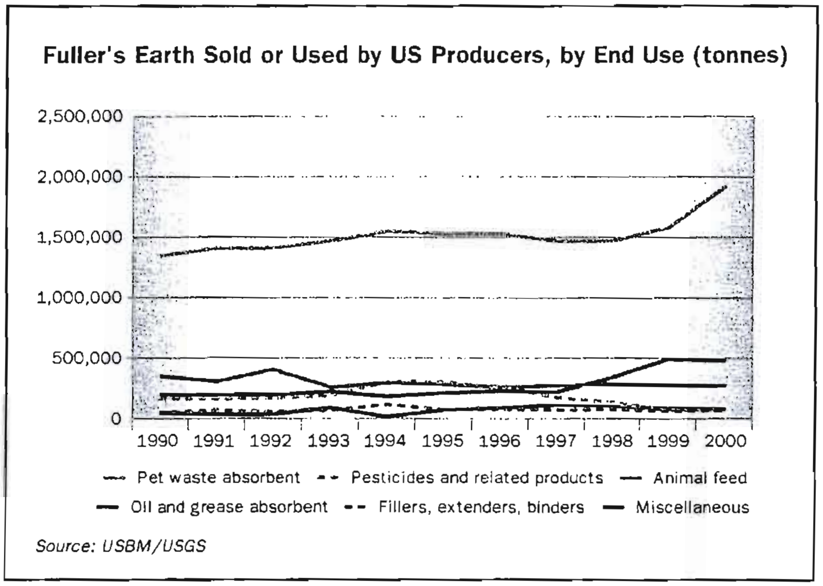
RECYCLING Virtually none, rather there is a disposal problem of spent product.

Requirements for Attapulgite & Sepiolite in Drilling Muds

Suspension properties, viscometer dial reading @ 600rpm	30 min.
Residue >75 μm	8.0 wt. % max.
Moisture	16.0 wt. % max.

Source: API Specification 13A, Specifications for Drilling-Fluid Materials, 1993

MARKET AND DRIVERS Demand for attapulgite and sepiolite depends on oil/gas drilling activity that is influenced by the price of oil and gas, the world economy, international politics, drilling conditions, and drilling technology. Drilling activity is highly volatile as shown by the rise and fall of the Baker Hughes rotary rig count (see *Barite and Barium Compounds* for recent activity). Since it requires less clay or uses polymer instead, the increased use of oil- and/or synthetic-based muds for deep and multi-directional drilling is reducing consumption of clays per meter of hole drilled. Capturing a significant share in the growing pet litter market has boosted demand, although sodium bentonite is the dominant clay in the popular "clumping" pet litter. However, blending plants close to the market has helped reduce the regional aspect of the market. The pet litter market is expected to grow irrespective of the prevailing economic conditions. In contrast, use as oil absorbents is expected to be static as oil-soaked residues are banned from some landfills. Bleaching clays are stable with little or no growth expected and animal feed should increase in line with GNP.



Fuller's Earth Sold or Used by US Producers, by End Use (tonnes)

Source: USBM/USGS

TRANSPORT AND PACKAGING Clays are available in 25kg bags, in bulk in pneumatic truck, hopper cars, or tote sacks, and packaged in absorbent socks, pads, and rolls. Activated clays in 25/50kg moisture-proof plastic woven bags with polyethylene liner (to avoid loss of activity) or 600/1,000kg jumbo bags.

PRICES With the exception of specialty gel grades, attapulgite prices have been flat for several years.

USA Attapulgite, FOT plant, Georgia, TL, bags $132-220/t (granular, 6/30 mesh), $360-690/t (specialty gel grades); $190-550/t (granular, processed, 40/100-4/8 mesh); $220-550/t (powder, 40-100% -325 mesh).

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Exhibit 26

CLAYS

An Overview

Colin C. Harvey and Haydn H. Murray

INTRODUCTION

The term *clay* is somewhat ambiguous unless specifically defined, because it is used in three ways:

- As a diverse group of fine-grained minerals
- As a rock term
- As a particle size term

As a rock term, clay is difficult to define because of the wide variety of materials that comprise it; therefore, the definition must be general. Grim (1962) defined clay as a fine-grained, natural, earthy, argillaceous material. The particle size of clays is very fine and is generally considered to be about 2 µm or less by most clay scientists. These minerals are hydrous silicates composed mainly of silica, alumina, and water. Several of these minerals also contain appreciable quantities of magnesium, iron, alkalis, and alkaline earths. Many definitions state that a clay is plastic when wet. Most clay materials do have this property, but some clays are not plastic, such as halloysite and flint clay.

As a particle size term, clay is used for the category that includes the smallest particles. The maximum size particles in the clay size grade are defined differently on various grade scales. Soil investigators and mineralogists generally use 2 µm as the maximum size, whereas the widely used scale by engineers (Wentworth 1922) defines clay as material finer than approximately 4 µm.

Some authorities find it convenient to use the term clay for any fine-grained, natural, earthy, argillaceous material (Grim 1968). When used in this way, the term includes clay, shale, argillite, and some fine soils.

Even though no standard definition of the term clay is accepted by geologists, agronomists, engineers, and others, the term is generally well understood by those who use it. Clay is an abundant natural raw material, and it has an amazing variety of uses and properties, which are discussed in the following chapters.

Clay Types and the Clay Chapters

The following seven chapters, written by experts on clay mineralogy, categorize the clay minerals on the basis of their composition:

- Ball clays
- Bentonite
- Common clays and shale
- Fuller's earth
- Kaolin
- Palygorskite and sepiolite (hormites)
- Refractory clays

There is some overlap between fuller's earth, bentonite, and hormites because they all have similar properties for some applications. Therefore, both the bentonite and palygorskite–sepiolite chapters discuss fuller's earth. *Fuller's earth* is a term based on use, and both bentonites and hormites may be sold as fuller's earth. The overlap is particularly evident where both bentonite and nonbentonite fuller's earth are used for the same purposes or products, such as in drilling mud, for bleaching or clarifying fats and oils, and as carriers for insecticides and fertilizers. Kaolin, ball clay, halloysite, and refractory clays are sometimes grouped together because they consist mainly of minerals of the kaolin group. Common clays have no unique mineral composition and may be composed of any mixture of the clay types and other fine-grained materials, including shale, sometimes referred to as miscellaneous clay.

WORLD PRODUCTION STATISTICS

Unfortunately no comprehensive world production statistics are available for the clay minerals. The U.S. Geological Survey (USGS; Virta 2003) publishes an annual review of statistical data but, unfortunately, numerous countries, including India and China, are not always included. Virta (personal communication) estimates that the recorded world production figure for kaolin reported by individual countries may also include the actual mined tonnage figures and does not take into account the losses incurred during processing. Although Virta (2003) quotes a world tonnage of 43 Mtpy of kaolin, he believes that the tonnage actually sold (raw plus processed) is closer to 26 Mtpy. His statistics, however, do not include China, India, and many former eastern bloc countries. Besides this estimate of world production of about 26 Mtpy of kaolin, other clay types include 10.3 Mtpy bentonite, 3.9 Mtpy of fuller's earth, and 13 Mtpy of ball clay, whereas hormite (palygorskite–sepiolite) production is estimated to be about 3 Mtpy.

The amount of common clays used worldwide is difficult to estimate since there are no comprehensive statistics. It is likely, however, to exceed many hundreds of million metric tons/year. Statistics for refractory clays also are not well documented. Their world production, however, exceeds 10 Mtpy and may indeed exceed 20 Mtpy. There are also a few unique deposits of high-purity clays such as halloysite (used in high-quality porcelain and catalysis) and hectorite (used in cosmetics and pharmaceuticals)

Table 1. World production estimates

Clay Type	2002 World Production, *Mt*	Reference
Common	Hundreds	Estimate only
Refractory	Possibly more than 20	Estimate only
Kaolin	43 mined	
	26 sold	Virta 2003
Bentonite	10.3	Virta 2003
Fuller's earth	Uncertain—possibly 10	
Ball	15.5	Chapter on Ball Clays in this volume
Hormites	2.1	Chapter on Palygorskite and Sepiolite in this volume

Table 2. Uses of clay minerals as inert components

Clay Family	Industry	Use
Kaolin	Paper, plastics, rubber	Filler
	Pesticides	Carrier, diluent
Vermiculite	Building	Heat insulation, sound dissipation
	Packaging	Shock-proof materials, thermal protection, liquid absorption
	Foundries	Thermal protection
Mica	Electrical	Insulation
	Paints	UV-, heat-stable and underwater paints
	Cosmetics	Nacreous pigments
	Coatings	Corrosion proofing, polymer coatings, underseal
Talcum, pyrophyllite	Plastics, rubber, paper	Filler
	Cosmetics, pharmaceuticals	Powders, pastes, ointments, lotions
	Refractories	Refractories
Palygorskite, sepiolite	Pesticides	Carrier for insecticides and herbicides
	Chemicals	Catalyst carrier, filter material, anticaking agent
	Cosmetics, plastics	Filler

that have unique properties leading to their classification as high-quality additives rather than bulk industrial minerals.

In addition, some nonclay minerals—finely ground to have similar properties to some industrial clays—are also frequently included in industrial clay surveys. These minerals include vermiculite, mica, talc, and pyrophyllite. The individual chapters present production statistics of the individual clays. Table 1 summarizes the estimated overall world production of clay minerals by both USGS sources and others.

CLAY USAGE

Clays and clay minerals are very important industrial minerals. They are used in many process industries, in agricultural applications, in engineering and construction, in environmental remediation, and in many other diverse applications (Grim 1962; Grim 1968; van Olphen 1977; Patterson and Murray 1983; Jepson 1984; Odom 1984; Murray 1986, 1999, 2000, 2003; Darley and Gray, 1991; Bundy 1993; Galan 1996; Harvey and Murray 1997; Ravichandran and Sivasankar 1997; and Philippakopoulou, Simonetis, and Economides 2003).

Table 3. Uses of clay minerals based on their rheological properties

Clay Family	Industry	Uses
Common clays	Ceramics	Tiles, bricks, earthenware, stoneware, sewer pipes, sanitary ware, refractory bricks
Kaolins	Paper	Coating
	Ceramics	Porcelain, bone china, vitreous sanitary ware, earthenware
Bentonites	See Table 4	
Palygorskite, sepiolite	Paints, chemicals, and mineral oils	Thickening and thixotropic additive, dispersing and antisettling agent, drilling fluids

Clay usage falls into two broad classes:

- Clays are used because their inertness and stability provide specific properties (such as unique rheology) to an industrial use. This leads to large variety of industrial applications.
- Clays are used because of their reactivity, which promotes or catalyzes specific reactions.

Tables 2, 3, 4, and 5 give a brief summary of uses; the individual chapters give a more detailed breakdown.

CLAY MINERAL STRUCTURES

All the clay minerals are basically hydrated aluminum silicates. There are, however, significant structural and chemical differences, which may include substitution of many cations that affect the neutrality or stability of the clay mineral. For example, iron or magnesium may substitute for aluminum; aluminum may substitute for silicon; and in some clay minerals, alkalis and alkaline earth elements are present as essential constituents. The structure of all the clay minerals consists of sheets of silicon tetrahedra and aluminum octahedra arranged in differing patterns for each individual clay mineral.

The physical properties of a particular clay mineral depend on the structure and composition (Murray 2000). Because of their extremely fine particle size, clay minerals were very difficult to identify until the advent of x-ray diffraction in the 1920s. Today, sophisticated analytical equipment is available to fully identify and characterize the clay minerals. The more important analytical methods that are used include x-ray diffraction, x-ray fluorescence, electron microscopy, infrared spectroscopy, and differential thermal analysis.

PHYSICAL AND CHEMICAL PROPERTIES

The important physical and chemical characteristics that relate to the applications of clay minerals are particle size, shape, and distribution; surface chemistry, area, and charge; pH; high and low shear viscosity; filter cake permeability; color and brightness; opacity; plasticity; green, dry, and fired strength; absorption and adsorption; fired color; electrical and heat conductivity; abrasion; cation and anion exchange capacity; refractoriness; dispersability; and thixotropy. The clay chapters each delineate and discuss these and other special properties. In most industrial applications, the clay materials are functional rather than just inert components in the system in which they are used. The common clays are the largest tonnage usage in numerous engineering applications, including road construction, fill, and dam construction, and in waste containment. The mineralogy and particle size distribution in the common clays determine their engineering properties. They contain mixtures of different clay minerals such as illite/smectite minerals, kaolinites,

Table 4. Uses of bentonites based on their rheological properties

Industry	Uses	Activation*
Agriculture, horticulture	Soil improvement	r, s
Building	Supporting dispersions for cut-off diaphragm wall construction, shield tunneling, subsoil sealing, antifriction agents for pipejacking and shaft sinking	r, s
	Additions to concrete and mortar	r, s
Ceramics	Plasticizing of organic masses, improvement of strength, fluxing agents	r, a
Foundries	Binding agents for molding and core sands	r, s
	Binding agents for anhydrous casting sands	o
	Thickening of blackwashes	o
Mineral oil	Drilling fluids	r, a, o
	Thickening of greases	o
Paints, varnishes	Thickening, thixotroping, stabilizing, antisettling agents	s, o
	Coating materials, sealing cement, additives for waxes and adhesives	s, o
Cosmetics, pharmaceuticals	Bases of creams, ointments, and cosmetics	r, a, s
	Stabilization of emulsions	r, o
Tar exploitation	Emulsification and thixotroping of tar-water emulsions	a, o
	Tar and asphalt coatings, additives for bitumen	

* Bentonites are used as raw materials or in activated form: r = raw bentonite, a = acid-activated bentonite, s = sodo-activated bentonite, o = organo-bentonite.

smectites, micas, and accessory minerals. A second class is termed *industrial kaolins*, which are recognized by their relatively high contents of kaolinite (kaolins) or sometimes a small proportion of high-quality kaolin minerals. Ball clays have very fine particle size and are composed predominantly of kaolin. A fourth class is clay that has a high montmorillonite (smectite) content (bentonites). A fifth class is the palygorskite and sepiolite clays (hormites), which have many similarities to bentonites and are used specifically for their surface properties and reactivity.

CLAY MINERAL SOCIETIES AND PUBLICATIONS

Several scientific societies and groups are devoted to the science and applications of clays. The major societies and groups that are currently active in clay science are as follows:

- The Clay Minerals Society in the United States
- The European Clay Group, which includes most of the European countries
- The Clay Science Society of Japan
- The Association Internationale pour l'Etude des Argiles (AIPEA)

Many of the individual clay groups in European countries hold meetings periodically. The Clay Minerals Society hosts an annual conference in the United States and publishes the journal *Clays and Clay Minerals*, plus special publications and workshop proceedings. The European Clay Group holds a Euroclay Conference every 2 years and publishes the journal *Clay Minerals*. The Clay Science Society of Japan sponsors an annual conference and publishes the journal *Clay Science*. AIPEA sponsors the International Clay Conference every 4 years and publishes the proceedings. The journal *Applied Clay Science* is published by Elsevier. Other organizations and publications that feature articles on clays are the American Ceramic Society (annual meetings and monthly bulletin); SME (annual meetings, preprints, *Mining Engineering* magazine, books, and transactions); and *Industrial Minerals* magazine.

Table 5. Uses of clay minerals based on their adsorption properties and reactivity

Clay Family	Industry	Uses
Kaolin	Fiberglass	Source of alumina
	Petrochemicals	Catalyst support
	Chemicals	Zeolite synthesis
	Building	Additive in cement
Bentonite	Agriculture, horticulture	Soil improvement, composting
		Adsorption of mycotoxins
	Chemicals	Sulfur production: refining, decoloration, bitumen extraction
		Catalysts
		Carriers for pesticides
		Dehydrating agents
		Adsorbents for radioactive materials
	Cleaning	Regeneration of organic fluids for dry cleaning
		Polishes and dressings
		Additives for washing and cleaning agents and soap production
	Environmental technology	Forest and water conservation: fire extinguishing powders, binding agents for oil on water
		Animal husbandry, manure treatment, cat litter
		Water and wastewater purification
		Sewage sludge pelletizing
		Barriers
	Food	Refining, decoloration, and stabilization of vegetable and animal oils and fats
		Fining of wine, must, and juices, beer stabilization, purification of saccharine juice and syrup
	Mineral oil	Refining, decoloration, purification, and stabilization of mineral oils, fats, waxes, and paraffins
	Papermaking	Pigment and color developer for carbonless copying paper
		Adsorption of impurities in circulation water
		De-inking in wastepaper recycling
	Cosmetics, pharmaceuticals	Powders, tablets, drug carrier, odor control, liquid absorption
Polygorskite, sepiolite	Chemicals	Adsorbent, carrier, bleaching, decoloration, anticaking agent
	Environmental technology	Cigarette filters (sepiolite), cat litter

The scientific and technological publications pertaining to clays are too numerous to cover in this chapter. Therefore, the rest of this chapter summarizes the subject matter and, where possible, indicates by bibliographic reference where more detailed information is available. For example, Bicker (1970) is a bulletin containing only summary information on the economic geology of bentonite in Mississippi, but it contains references to virtually all published reports on bentonite in that state.

Major textbooks and reference volumes on various aspects of clay mineralogy and the industrial uses for clay published in the last 5 decades include Mackenzie (1957), Grim (1962, 1968), Zvyagin (1967), Beutelspacher and Van Der Marel (1968), Gillott (1968), Clews (1969), Malkovský and Vachti (1969a, 1969b, 1969c), Carroll (1970), Gard (1971), Weaver and Beck (1971), Grimshaw (1972), Weaver and Pollard (1973), van Olphen (1977), Theng (1979), Brindley and Brown (1980), Velde (1985), Robertson (1986), Newman (1987), Bailey (1988), Chamley (1989), Murray, Bundy, and Harvey (1993), Moore and Reynolds (1997), Pinnavaia and Beall (2000), Worden and Morad (2003), and Kloprogge (2005). Many other excellent books on clays could be mentioned. Various provincial, state, and federal geological surveys, mining bureaus, and other international agencies have also published much information on the geology, technology, and uses of clay.

Within the United States several industrial groups with similar industrial processes and markets have formed institutes or associations to share information, standardize specifications and test procedures, and lobby government or trade organizations for support. They include the following:

- The Sorptive Minerals Institute, formed mainly to represent the producers of absorbent granules and other fuller's earth products
- The Bentonite Producers Association, organized to represent the interests of the producers of bentonite
- The U.S. Clay Producers Traffic Association, incorporated in 1953 in New Jersey
- The China Clay Producers Association

In addition to these organizations dealing specifically with clays, the clay industry and other mining industries formed mining associations in many states, including Georgia and Texas in 1972, to protect their interests against restrictive state and federal legislation.

OCCURRENCE OF CLAY MINERALS

Clay resources may be formed from weathering processes, diagenesis, metamorphism, or hydrothermal processes. The nature of the formation process significantly affects the crystallinity and purity of the clay and its associated minerals. Resources that are still in situ after the formation processes are termed *primary clay resources* whereas, if subsequent erosion, sorting, and sedimentation occur, thereby concentrating the finer clay minerals, the resources are termed *secondary clay resources.* The origin of all clay types is discussed under the individual clay chapters. Pure clays do not usually occur in nature.

TECHNOLOGIES FOR CLAY PROCESSING

The processing technologies for clays are diverse. Many clays are used as mined, some are dry processed using air classification, whereas others are wet processed, chemically modified, or processed using a variety of complex processing steps. The individual clay chapters discuss these processes.

CATEGORIZATION OF CLAY RESOURCES

With the continued world population growth and movement toward urbanization and industrialization, there is an ongoing and growing need throughout the world to develop resources of industrial clays. During the early to middle part of the 20th century, developments in the industrialized world typically began on a small scale from a low technology base. The initial market focus was on construction materials or relatively low-quality ceramic products. With increasing levels of industrialization, the level of technology and product sophistication increased, with the ultimate objective of achieving high product quality.

Over the past 20 years, the developed world has experienced the following:

- The exhaustion of many natural resources
- Mature low-growth markets
- Increasing environmental constraints
- Higher labor costs
- A general movement against mining in many countries

This has encouraged interest and investment in resources in developing nations. In addition, growth in the gross domestic product (GDP) of many developing nations has provided investment capital for the development of their indigenous clay mineral resources.

On the basis of many industrial clay mineral studies in both developed and developing countries, it has been found that categorizing industrial clays into one of four categories is a useful precursor to undertaking technical and economic evaluations of potential resources. Such categorization also benefits the explorer or developer because it:

- Assists in identifying the most suitable development strategy
- Provides a general estimate of the time required to move from greenfield development to production
- Enables a work program to be broadly defined
- Permits provisional project cost estimates to be made

Categories of Industrial Clays

Clay resources fall in to four categories (Harvey and Murray 1997):

- Category 1 clays are high-quality, high-technology clays requiring major investment for large tonnage production to supply both local and international markets.
- Category 2 clays are unique specialty clays requiring advanced technologies for small tonnage niche markets, locally and internationally.
- Category 3 clays include low-technology, moderate-quality clays that mainly supply local markets.
- Category 4 clays are of variable quality.

Category 4 low-quality clays may justify little or no processing but be suitable for large tonnage local markets. Some Category 4 clays may be of moderate to high quality but for one or more reasons are considered noneconomic. These reasons may include:

- Isolation from markets
- Politically or economically unstable locations
- Unfavorable legislative environment

Examples of Different Categories

Category 1

Three regions (kaolin provinces) currently produce Category 1 kaolin clays:

- The sedimentary kaolins of southeastern Georgia in the United States
- The hydrothermal kaolins of Cornwall in the United Kingdom
- The sedimentary kaolins of the Amazon Basin in Brazil

The limited number of kaolin resources identified in this category confirms the rarity of Category 1 clays currently known worldwide. They are discussed in detail in the Kaolin chapter.

Category 2

There are also very few resources that might be classified as Category 2. These are relatively rare, unique resources of somewhat unusual, but valuable industrial clay minerals. Such deposits are typically of high purity and are found in somewhat unique geological settings. Examples include the halloysite deposits of New Zealand, which are unusually pure deposits of halloysite formed by low-temperature hydrothermal alteration of volcanic ash (Harvey and Murray 1993, Harvey 1996). Halloysite is wet processed and supplied to a unique niche market in high-quality ceramics.

A second example is hectorite, a lithium smectite that also is the product of hydrothermal alteration. In this case, basaltic ash with elevated concentrations of magnesium and lithium was subjected to hydrothermal alteration, forming this lithium smectite (bentonite). It is wet or dry processed and used in a wide variety of industries (coatings, greases, adhesives, and paints) because of its high viscosity, high gel strength, and good temperature stability.

A third example is white bentonite, which is very rare in nature and commands high prices in colloid applications, detergents, pharmaceuticals, and ceramics. For some specialty markets, these bentonites are wet processed or surface modified to achieve the high quality required for such applications.

Category 3

Category 3 resources are numerous and widespread. Their specifications are typically not rigid, which means that the level of processing is typically only moderate because the market quality requirements and pricing cannot justify high processing costs. All of the known Category 1 resources around the world also contain large tonnages of these clays, which are too impure to meet Category 1 requirements. Examples of large exploited resources of Category 3 clays associated with Category 1 clays are the filler kaolins of Georgia (United States) and of Cornwall (United Kingdom). Other Category 3 resources contain few if any Category 1 component. These include the kaolin resources of Central Europe in the Czech Republic, Ukraine, and Germany; the filler grade kaolins of Indonesia; and the bentonite resources of Wyoming and the southeastern United States.

An example of a Category 3 clay is the Belitung kaolins of Indonesia. During the 1960s and early 1970s these primary kaolins were mined as an adjunct to the associated, highly profitable, tin mining operations. With the radical drop in tin prices during the 1970s and 1980s, more emphasis was placed on the kaolin operations. These clays are currently exploited to supply large ceramic and filler clay markets within Indonesia and they are also exported to Asian countries, including Taiwan, Japan, and South Korea.

Category 4

Category 4 clays exist in all countries of the world and are typically used as mined.

Role of Categorization in Assessing Industrial Clay Resources

In any assessment of an industrial clay resource the explorer or developer has to go through the various stages of resource assessment, raw material testing, and assessment of product quality, market size, and market demand. All these data must then be integrated into a feasibility study that will recommend whether the project should proceed or be abandoned. An early classification of materials into one or more of the four categories can be a useful precursor to establishing development strategies and likely project costs. Such categorization can provide a useful insight into the complexities of such studies because these different categories have different requirements for the work program needed and the time frame to reach the feasibility study.

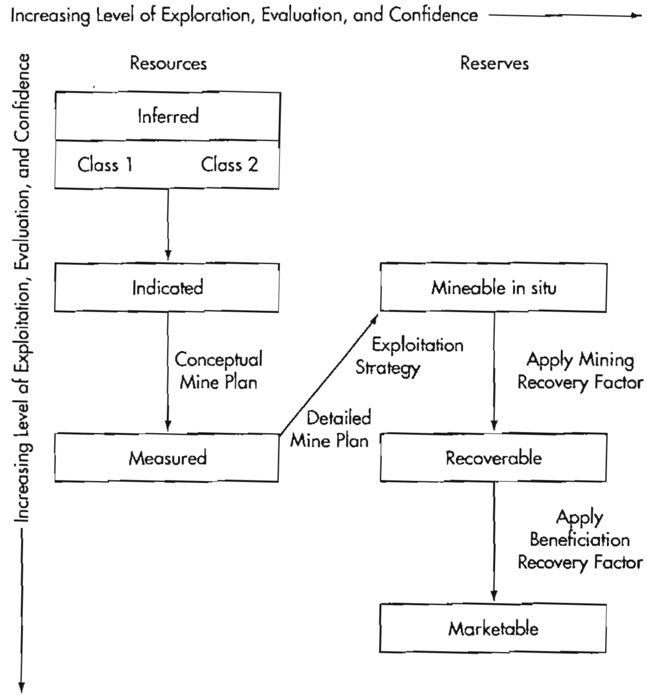

Figure 1. Flow chart showing levels of confidence and assessment of mineral resources and reserves

Relationship between Category and Annual Tonnage

In any mineral processing operation, the term *benefits of scale* is used to indicate that significant economic advantages can be obtained by having larger production volumes and by shipping in larger vessels. Larger tonnage operations operate with fewer labor hours per ton whereas capital costs for larger machines are less than the multiples of their relative production capacities. To compete on world markets, Category 1 producers must consider the benefits of scale. In the kaolin industry in the 1970s, for example, a 100,000 tpy operation was considered a reasonable commercial operation. For the current developments in Brazil, a minimum plant size of 300,000 tpy is being quoted. Category 2 clays have annual tonnage requirements that are governed by market size rather than benefits of scale. Annual production from such processing operations typically falls between 10,000 and 100,000 tpy. The sizes of Category 3 operations are typically governed by factors such as market size or accessible market share.

Relationship between Category and Resource Confidence

Based on the category criteria, the development of a Category 1 resource requires a very high level of confidence in the quality and quantity of the raw material. If a minimum resource life of 20 years is required at 300,000 tpy, then the resource must be of sufficient size to produce 6 Mt of product. For Category 2 and Category 3 industrial clays, the tonnage requirements may be significantly less and resource confidence may also be less.

Figure 1 shows the various levels of resource certainty that are internationally recognized in the classification of industrial mineral resources.

The lowest level of confidence (*Inferred*, in the upper left corner), exists when no drilling or detailed testing has been carried out. The level of confidence moves from *Inferred* to *Indicated* when an initial exploration and testing program has been carried

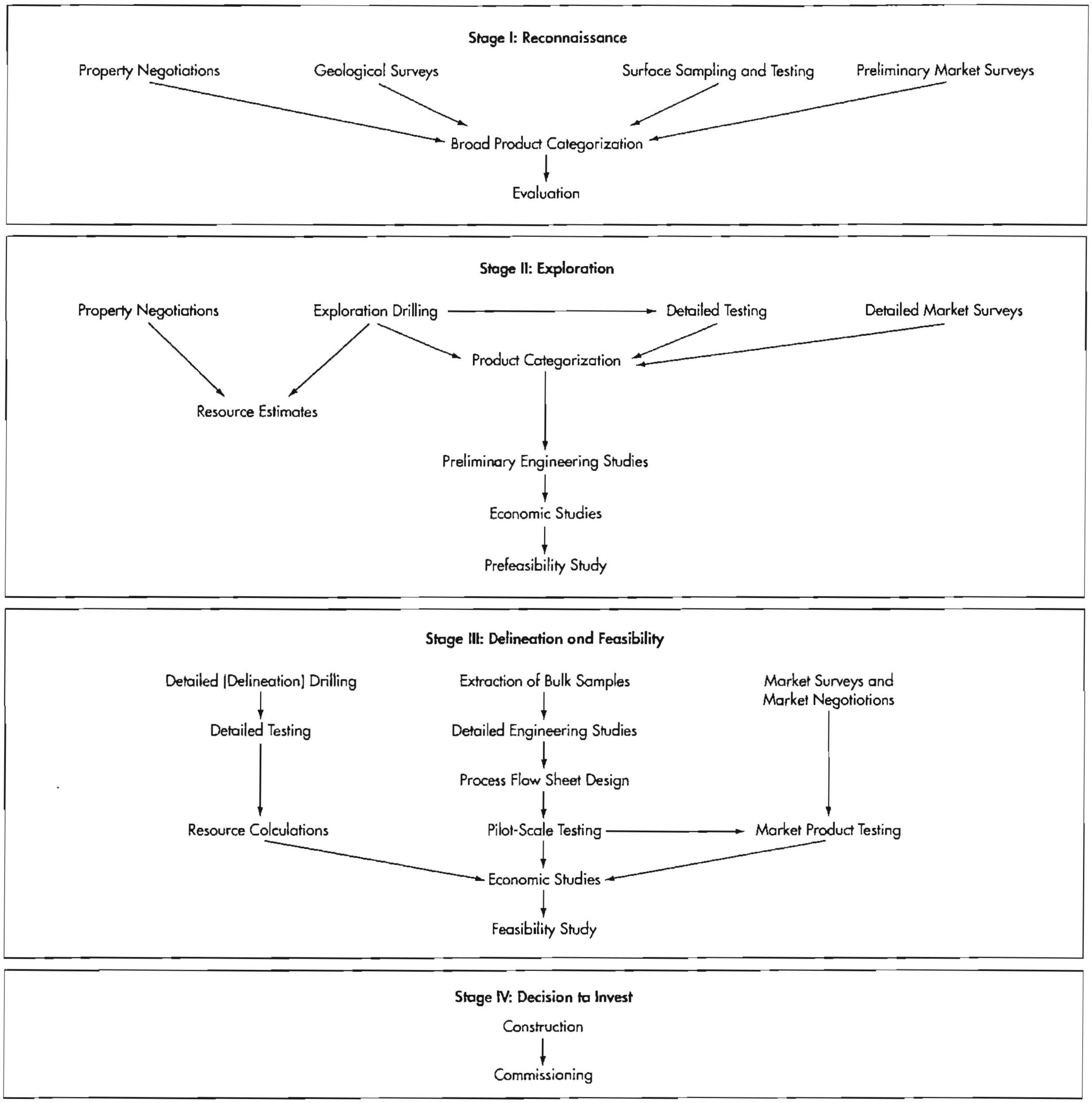

Figure 2. Flowsheet of project development

out and the boundaries of the resource in three dimensions may be reasonably estimated. Once a systematic exploration, drilling, and testing program has been completed, the level of confidence moves to *Measured.*

This may result in a prefeasibility study when a decision is made to proceed or withdraw from the project. If the project proceeds, then further drilling and testing leads to a mine plan, exploitation strategy, and calculations of *Mineable in situ* tonnages. A recovery figure for mining and processing may then be applied to calculate the *Recoverable* and *Marketable* reserves.

For resources in Categories 1 and 2 it is essential that the knowledge be at the Marketable reserves stage. For Category 3 minerals, the resource certainty may be much less, possibly at the *Inferred* resource level or less.

Relationship between Category and Value

Category 1 kaolin products command the largest tonnage and highest added-value positions in the industry. Frequently, however, it is the Category 2 products that command the highest unit value position, although their tonnages may be relatively small. Category 3 kaolins command an intermediate value between Category 1 and Category 4 kaolins.

Relationship between Category and Preinvestment Capital

Category 1 projects require significant preinvestment or "risk" capital. The level of confidence in the resource and markets has to be very high, requiring a significant level of investment that may well exceed US$1 million. The payback time for such investments can be at least 5 years because of the time required to move from reconnaissance to commissioning. The preinvestment capital requirements for Categories 2, 3, and 4 become progressively lower as the category of clay moves lower.

Relationship between Category and Investment Capital

The investment capital requirements for large tonnage, high-complexity Category 1 kaolin projects are quoted to be as high as US$300 per processed ton (Harvey 1995; Pleeth 1997). For Category 2 kaolins, investment capital costs would depend on the complexity of the process but might range between US$100 and US$500 per processed ton. For Category 3 kaolins, the investment level may be less than US$50 per finished ton.

THE RESOURCE EVALUATION PROCESS

The evaluation moves through a series of progressively more detailed stages as shown in Figure 2.

Translating from Laboratory-Scale Testing to Major Plant Scale

The clay industry has many examples of insufficient scale-up factors being applied to basic laboratory data. This ranges from basic recovery figures to assessments of product quality based on too few laboratory test data. For example, losses during commercial plant operations may be much higher than in small-scale laboratory test equipment. A conservative approach to both laboratory- and pilot-scale test data is essential.

The Level of Applied Technology

Almost anything can be done with a low-grade clay resource if a sufficient number of applied technologies are thrown at it. For example, with commercial kaolin resources, a wide-ranging selection of technologies can be applied. By applying a number of such technologies to a low-grade raw material, it may be possible to upgrade it significantly. When all the various processes are costed into the operation, however, the total expenditures (and process losses) may become prohibitive, effectively constraining development of the resource.

Losses Associated with Applied Processing Steps

For each technology introduced into a process there will be process losses. These may range from 2% to much higher values. If, however, it is generalized that each process step loses 4% of product, then the effects of multistage processing on recoveries may be very significant. Also, such losses will be cumulative.

Time to Move from Commissioning to Full Production

Industries that use industrial minerals are often conservative by nature and do not readily accept new products. For example, the paper industry uses a complex technology, and an industrial clay such as kaolin may be just one component in a complex formulation. Purchasing agents may have to be convinced that the product is compatible with their formulations, and further, that the product quality and supply will be consistent. To reach this stage, it is necessary to convince the company of the quality, consistency, and value of a new product over and above the quality of its existing supplier. In such cases it may be necessary to compete on the basis of higher quality, lower price, better continuity, or better technical support. Even with such strengths, however, the new player in the marketplace still has to deal with buyer conservatism. Therefore, the rate at which a product is accepted may be a combination of advantageous positioning and sheer luck. For some products, it may take years to gain full market acceptance. For example, recent developments of Category 1 kaolin resources in Brazil (Pleeth 1997) quote time intervals of at least 5 years to move from initial exploration through to commissioning. Table 6 illustrates typical times required.

Table 6. Timetable of activities and investments

	Category			
Activity	**1**	**2**	**3**	**4**
Stage I: Reconnaissance				
Geological reconnaissance, property surveys, testing, broad categorization of materials, market surveys and evaluation				
Decision to proceed (months)	12	9	6	3
Stage II: Exploration (prefeasibility)				
Property negotiation, drilling, testing, market surveys, precise material characterizations, process flowsheet development, resource calculations, economic studies and evaluation				
Prefeasibility study and decision to proceed (months)	18–24	9	9	6
Stage III: Delineation and feasibility				
Drilling, testing, market surveys, bulk samples, engineering studies, assessment of products in the marketplace, economic studies and evaluation				
Feasibility study (months)	24	12	9	3
Stage IV: Decision to invest				
Total elapsed time since project initiation (years)	4–5	2.0–2.5	2	1
Design, construction, and commissioning (years)	1–2	1	1	1
Typical overall project time (years)	5–7	3–4	2–3	1

Reducing Risk during Development

There are several procedures for minimizing risk and reducing the time necessary to develop Category 1 or Category 2 ventures:

- Associate or form a joint venture with established producers in the industry.
- Associate or form a joint venture with major market users of the product.
- Engage specialized consultants for resource evaluation, market surveys, and so forth.
- Develop resources adjacent to proven established resources.

SUMMARY

This overview illustrates the diverse nature of clay minerals and the breadth of their technologies and markets, and demonstrates why they are such important industrial minerals. The seven chapters that follow expand on the individual clay types.

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Exhibit 27

MAY -1 2009

CLAYS

Palygorskite and Sepiolite (Hormites)*

Haydn H. Murray and Huitang Zhou

INTRODUCTION

The hormite clay minerals palygorskite and sepiolite are elongate clays that have many important industrial applications. Important deposits of these clays occur in the United States, China, Senegal, Spain, India, and Ukraine. The majority of the deposits are Miocene in age. Mining is by open-pit methods, and the processing is dry, although there is some wet processing for special applications.

Palygorskite and sepiolite are hydrated magnesium, iron, and aluminum silicates. In the United States, the term *attapulgite* is used in place of palygorskite; however, the International Nomenclature Committee determined that palygorskite is the preferred name (Bailey et al. 1971).

In 1862, Savchenkov used the name "palygorskite" to describe a mineral from the Palygorsk locality in the Ural Mountains (Hay 1975). J. deLapparent proposed the name "attapulgite" for clays from Attapulgus, Georgia, in the United States, and from Mormoiron in France, because he thought them to be different than palygorskite, but Bailey et al. (1971) proved them to be the same.

Both palygorskite and sepiolite are referred to as sorptive clays because of their large surface area and high sorptive capacity. The term *fuller's earth* adds additional complications to the nomenclature. Fuller's earth is more or less a catchall term for clays and other fine-grained earthy materials suitable for bleaching and sorbent uses. It has no compositional or mineralogical meaning. Fuller's earth was first applied to earthy materials used in cleansing and fulling wool, thereby removing lanolin and dirt—thus the name fuller's earth (Robertson 1986). The term "fuller's earth" is used quite often for palygorskite and sepiolite, some smectites, and other sorptive materials. For more detailed information, refer to the chapter on fuller's earth elsewhere in this volume.

Because of the elongate shape of palygorskite and sepiolite, the industrial applications are many and diverse. The elongate shape of the particles prevents flocculation, so these clays are used as suspending agents in systems with high electrolyte concentrations.

MINERALOGY, OCCURRENCE, AND ORIGIN

Mineralogy

Both palygorskite and sepiolite are 2:1 layer silicates, which means that the octahedral layer is bound above and below by a silica tetrahedral sheet. The tetrahedral sheets are linked infinitely in two dimensions. These two minerals are structurally different from other clay minerals in that the octahedral sheets extend in only one dimension and the tetrahedral sheets are divided into ribbons by a periodic inversion of rows of tetrahedrons. Figure 1 shows the structure of palygorskite (attapulgite) and Figure 2 shows the structure of sepiolite; the channels between the ribbon strips are larger in sepiolite than in palygorskite. In palygorskite the dimensions of the channels are approximately 4 Å by 6 Å and in sepiolite the dimensions are about 4 Å by 9.5 Å. Figure 3 shows a scanning electron micrograph (SEM) of palygorskite. The general chemical formula for palygorskite is Mg_5 (Si_8O_{20}) $(OH)_2$ $(OH_2)_4 \cdot 4H_2O$ and for sepiolite is Mg_8 $(Si_{12}O_{30})$ $(OH)_4$ $(OH_2)_4 \cdot N\ H_2O$.

These two clay minerals contain two types of water—one coordinated to the octahedral cations and the other loosely bonded in the channels. The latter water is referred to as zeolitic water. The channels may also contain exchangeable cations. The elongate morphology and the presence of the channels are the most important physical attributes, which are described later in this chapter.

Palygorskite is more common than sepiolite. Usually, minor quantities of sepiolite are associated with the palygorskite. The major exception is the large sepiolite deposit near Madrid in Spain. Minor minerals in these deposits are smectite, quartz, dolomite, calcite, and occasionally clinoptilolite.

Bradley (1940) determined the structure of palygorskite and Brauner and Preisinger (1956) determined the structure of sepiolite. Merkl (1989) in his study of the palygorskite deposits in south Georgia and north Florida observed two distinct morphological forms: short-length palygorskite and long-length palygorskite. The short form is 2 µm or less, and the long-length form is greater than 10 µm. He determined that the short-length form had a low magnesium content, whereas the long-length form had a high magnesium content.

Origin and Occurrence

The important deposits of palygorskite and sepiolite occur in southeastern United States, China, Senegal, Spain, and Ukraine (Figure 4). All these major deposits are Eocene or Miocene in age. The origin of these deposits is somewhat uncertain, but in

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* At the 13th International Clay Conference held in August, 2005, in Tokyo, the International Nomenclature Committee recommended that use of the term "hormites" be discontinued and all future references be replaced with palygorskite and sepiolite. Therefore, this chapter, originally titled "Hormites," has been renamed "Palygorskite and Sepiolite" and references to hormites throughout the chapter have been replaced with palygorskite and sepiolite.

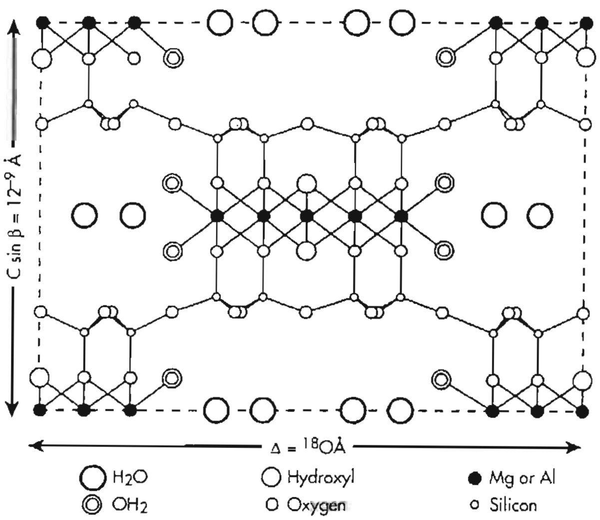

Figure 1. Structure of polygorskite

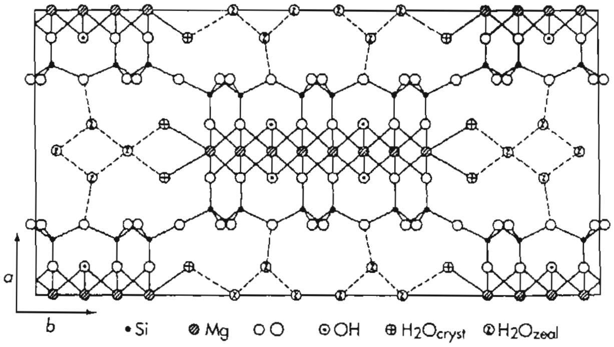

Figure 2. Structure of sepiolite

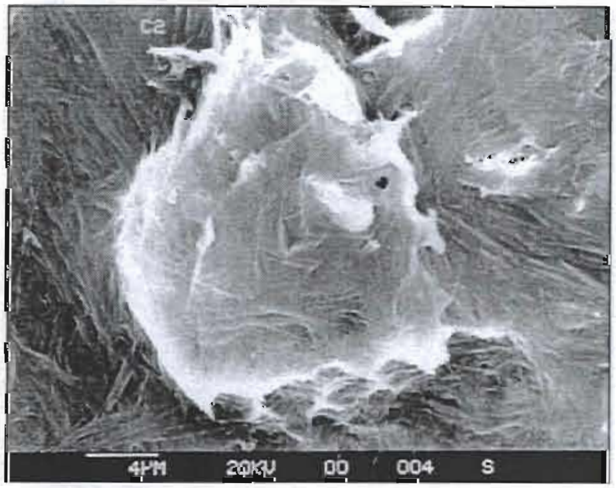

Figure 3. SEM of palygorskite

general most formed in shallow marine lagoons or tidal flats and in supersaline lakes. The magnesium needed to form the palygorskite, sepiolite, and dolomite was apparently introduced by the reaction of detrital material with magnesium-rich brines and salts resulting from the evaporation of the entrapped sea water (Patterson 1974). The palygorskite and sepiolite precipitated in these hypersaline restricted lagoons or lakes. The dolomite formed under conditions in which the amount of aluminum and silicon was less available from the clastic materials that entered the basin (Weaver and Beck 1972).

United States

The palygorskite-rich deposits in south Georgia and north Florida dominate the world's production. The deposits extend from Quincy, Florida, on the south to the Meigs, Georgia, area on the north (Figure 5), about 80 km. The deposition of the palygorskite took place in a shallow water trough that connected the Gulf of Mexico with the Southeast Georgia Embayment on the Atlantic Ocean (Merkl 1989). The seawater in this trough was characterized by fluctuating salinities, and at times the lagoons were closed off from normal circulation. There was sufficient magnesium present to precipitate palygorskite. The mineralogical content changes from dominantly palygorskite in the Quincy–Attapulgus District to a mixture of smectite and palygorskite in the northern area around Ochlocknee and Meigs. Millot (1970) believes that smectite is transformed to palygorskite and sepiolite in a saline, alkaline water environment. These Georgia–Florida deposits are early to middle Miocene in age.

The palygorskite-type fuller's earth occurs in two distinct stratigraphic intervals. The younger Meigs Member of early middle Miocene age unconformably overlies the Dogtown Clay Member of late Lower Miocene age (Figure 6). Both of these members are part of the Hawthorne Group. The Meigs Member contains about equal proportions of smectite and short-length palygorskite along with quartz and a small amount of sepiolite, Opal-A, and sporadic amounts of clinoptilolite. In some sections of the deposit, diatoms comprise up to 50% or more of the fabric. The Dogtown Member has longer length palygorskite and minor amounts of quartz, smectite, and dolomite along with trace amounts of pyrite (Merkl 1989). The deposits in the Dogtown Clay Member in the southern district range from 2 m to slightly more than 3 m in thickness. The deposits in the Meigs Member in the northern district near Ochlocknee and Meigs range from 9 to 14 m in thickness.

Sepiolite is mined in small quantities near Lathrop Wells, Nevada, about 160 km northwest of Las Vegas in the Amargosa Valley. The sepiolite occurs in thin beds less than 1 m thick interbedded with deposits of saponite. These deposits are Pleistocene in age (Papke 1969).

China

Palygorskite is mined and processed in an area located near the provincial boundary of Anhui and Jiangsu near Guanshan and Xuyi, respectively (Figure 7). At the Guanshan deposit, the palygorskite occurs directly beneath a thick basalt. The palygorskite ranges between 3 and 6 m in thickness (Zhou and Murray 2003). The palygorskite in the Guanshan deposit was precipitated in a lacustrine environment as the alteration product of a basaltic ash (Zhou 1996). The deposits are in the upper member of the Huaguoshan Formation, which is Middle Miocene in age (Figure 7). Within the last 20 years, more than 20 high-quality palygorskite deposits have been discovered in the area shown in Figure 7. The Geological Survey of China estimated that there are more than 200 Mt of palygorskite reserves in this area. The mineralogy of these deposits is dominantly

Figure 4. Location of major palygorskite and sepiolite deposits

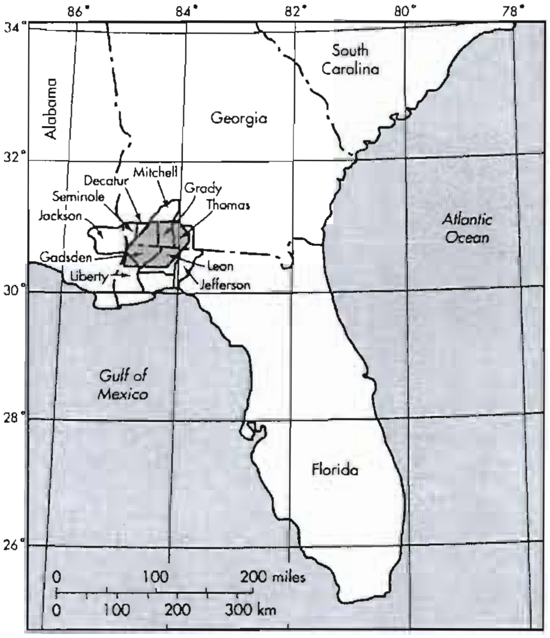

Figure 5. Location of the south Georgia–north Florida fuller's earth deposits

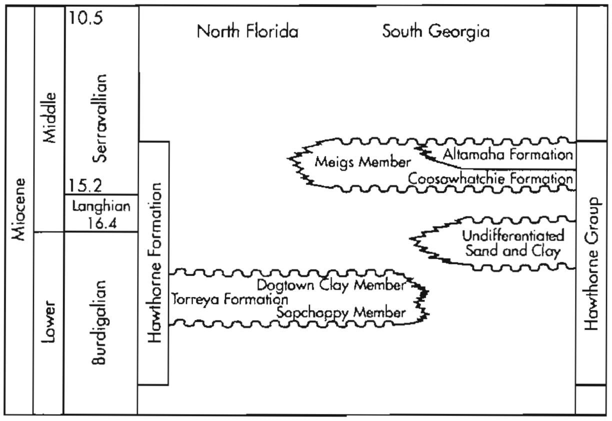

Figure 6. Stratigraphic relationship of the Meigs Clay and Dogtown Clay members

palygorskite with minor amounts of smectite, quartz, and dolomite. In the Guanshan deposit, the smectite content increases significantly below the palygorskite layer.

Senegal

Palygorskite is mined near the town of Theis, Senegal, which is approximately 100 km east of Dakar. In this area, the palygorskite directly overlies an aluminum phosphate deposit that is also mined. The age of the palygorskite is Early Eocene, and the beds range from 2 to 6 m in thickness (Wirth 1968). The palygorskite is transported by truck to Dakar, and the majority is shipped to Europe. It is estimated that about 400 kt are processed and shipped annually. The palygorskite is used for industrial absorbents, pet litter, and drilling mud mainly in the North Sea. The deposits are palygorskite along with minor amounts of sepiolite, quartz, and dolomite. The palygorskite beds extend south–southwest from Theis to the southern border of Senegal, a distance of about 100 km. The overburden is very thin, usually less than 2 m.

Spain

The world's major commercial sepiolite deposit is located at Vicalvaro near Madrid. The sepiolite was precipitated in Tertiary lakes in an evaporitic sequence (Huertas, Limares, and Martin-Vivaldi 1971). The thickness ranges from 1 to 5 m. The major uses for this

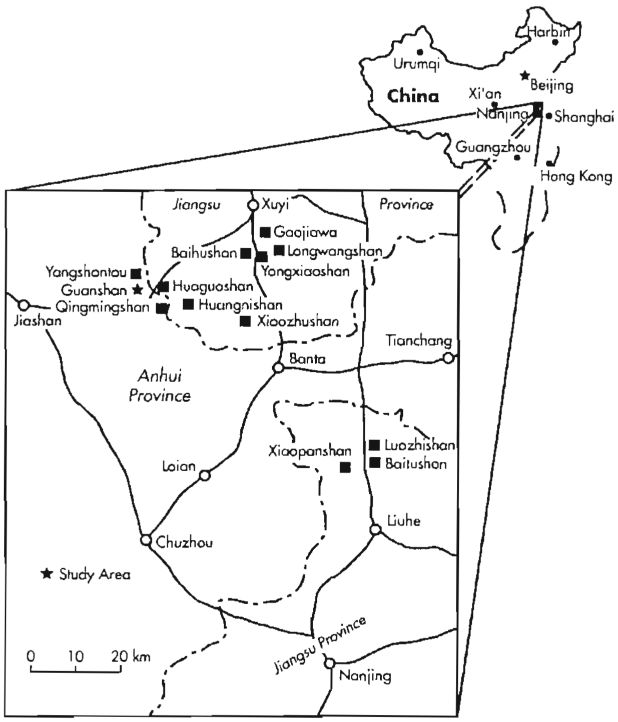

Figure 7. Location of palygorskite deposits in China

sepiolite are pet litter, agricultural carriers, and drilling mud. Approximately 500,000 t are produced annually from the deposits at Vicalvaro. Other locations in Spain producing palygorskite and sepiolite are Toledo, Torrejon el Ruhe, Lebija, Almeria, and Maderuelo (Griffiths 1991). Galan (1996) reviewed the properties and applications of the these clays and showed the relationship between the structure, composition, and physical properties and their industrial applications. Galan et al. (1976) described a deposit of palygorskite in the province of Caceres. In addition to the applications previously mentioned, palygorskite and sepiolite are used in plastics, mastics, catalysts, bleaching earth, ceramics, and binders for animal feed.

Ukraine

Ovcharenko et al. (1964) described large deposits of palygorskite of Lower Miocene age. Near Kiev, Ukraine, in the Cherkassey District, palygorskite is mined primarily for use in drilling muds. The palygorskite in Ukraine occurs in the central portion of the Ukrainian crystalline massif in the regions near Cherkassey and Kiev. The palygorskite-rich bed occurs in the middle section of a bentonite deposit and is Lower Miocene in age (Ovcharenko and Kukovsky 1984). The thickness of the palygorskite layer is approximately 2 m. Smectite, hydromica, and quartz are the other mineral constituents in the palygorskite-rich layer.

Other Locations

Palygorskite occurs in Western Australia in a surface deposit at Lake Marromyne. In Turkey, sepiolite is produced near Eskisehir in Anatolia. In Somalia, a deposit of sepiolite is used mainly to produce decorative carvings that are sold to tourists. In Guatemala, there is a deposit of palygorskite about 40 km from the Gulf of Mexico and 30 km south of the Belize border.

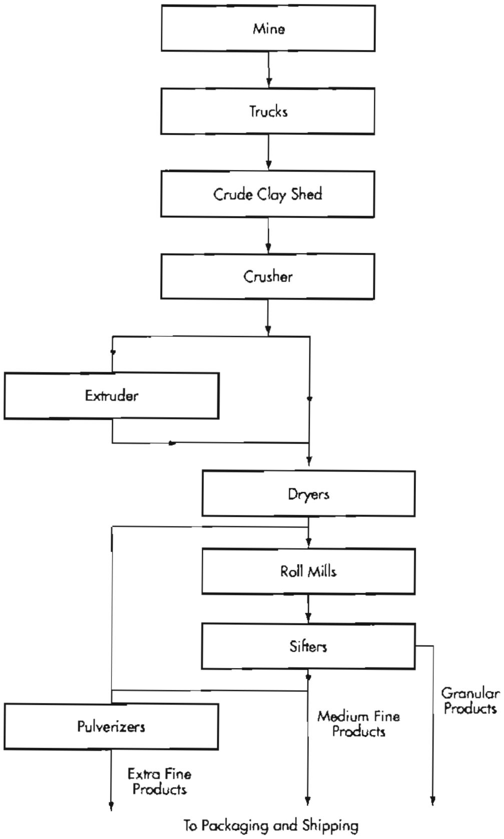

Figure 8. Process flow sheet for palygorskite and sepiolite production

MINING AND PROCESSING

Palygorskite and sepiolite are surface mined. The overburden is stripped with motorized scrapers, draglines, shovels, or bulldozers. The clay is mined using shovels, backhoes, small draglines, or front-end loaders, and is then loaded in trucks that transport the clay to the processing plant. The processing is generally quite simple, involving crushing, drying, classification, and pulverizing. Figure 8 shows a general process flow sheet. Special processes to enhance certain properties are sometimes used, including extrusion to separate the elongate particles; adding 1% or 2% MgO to improve the viscosity for use in drilling muds or thickeners; high heat drying to remove the zeolitic water from the channels in the structure, which produces LVM (low-volatile material) that improves the sorbent properties; and ultrafine pulverization to improve suspension properties and increase the surface area for use in certain pharmaceutical and paint applications. Some palygorskites are acid activated to enhance their bleaching activity for use in clarifying edible and nonedible oils. This acid activation process can be dry, or wet if a superior bleaching earth is required.

Pet litter and agricultural absorbents are granular products that are produced by drying, roll crushing, and screening to a specific granular size. The granular products generally are 15/30, 30/60, and 60/90. This means that the granule passes through the first number and is retained on the second number. A 15/30 product means that all the granules range between 15 and 30 mesh.

PHYSICAL PROPERTIES AND APPLICATIONS

Particle size, shape, distribution, surface area, chemistry, and charge are important physical properties that relate to the application of palygorskite and sepiolite. The properties of these clays that relate to their applications are

- 2:1 layer and inverted structure
- Octahedral substitutions (Mg, Fe, Al)
- Moderate charge on the lattice
- Moderate base exchange capacity (30 to 50 meq/100 g)
- Elongate shape
- Specific gravity 2.0–2.3 g/cm^3
- Mohs hardness 2.0–2.5
- High surface area (150 to 320 m^2/g)
- High absorption capacity
- High viscosity
- API (American Petroleum Institute) yield—100 to 115 bbl/t

The most important physical property of these clays is their elongate shape, because in many applications it is the controlling property. Considerable substitution of aluminum by magnesium and iron in the octahedral layer gives the particles a moderately high surface charge. This surface charge and the high surface area give the clays a moderate exchange capacity normally ranging from 30 to 50 meq/100 g. The large surface area of more than 100 m^2/g, the charge on the lattice, and the periodic inverted silica tetrahedra, which creates parallel channels in the lattice, give paylgorskite and sepiolite a high sorptive capacity. These properties, along with the elongate habit of the minerals, make them very useful in many industrial applications. The high viscosity of liquids into which these clays are added is a physical rather than a chemical viscosity, which makes for a very stable suspension viscosity.

The more important industrial applications of palygorskite and sepiolite follow:

- Adhesives
- Agricultural carriers
- Animal feed bondants
- Anticaking agent
- Catalyst supports
- Decolorizing oils
- Drilling fluids
- Environmental liners
- Foundry sand binders
- Granular carriers
- Industrial floor absorbents
- Laundry washing powders
- Metal drawing lubricants
- Paint and coatings
- Paper
- Pet litter
- Pharmaceuticals
- Polishes
- Reinforcing fillers
- Suspension fertilizers
- Tape joint compounds
- Wax emulsions

One of the more important and larger uses is in drilling fluids, where both the viscosity and the gel strength of the mud are not affected by variations in electrolyte content as are drilling muds in which bentonite is used. Palygorskite and sepiolite drilling muds can be used with salt water or when formation brines become a serious problem. The specifications for their use (API Specification 13A) in drilling mud follow. These measurements are made in water containing 40 g of salt (NaCl) per 100 cc of water.

- Viscosity—30 centipoise minimum at 600 rpm
- Yield point/plastic viscosity ratio—3 maximum
- Filtrate volume—15 cm^3 maximum
- Residue—75 µm—4.0 wt % maximum

Table 1. Annual 2004 world production of palygorskite and sepiolite, *st*

United States	1,200,000
Spain	900,000
Senegal	150,000
China	70,000
India	60,000
Others	100,000
Total	2,480,000

The clays are not flocculated because of their elongate particle shape, and thus they are used as suspending agents and thickeners in paint, medicines, pharmaceuticals, and cosmetics. Ultrafine pulverization to 95% less than 10 µm substantially improves the suspension properties. Another large use is as floor-sweep compounds that absorb oil and grease spills on factory and service station floors and in other areas where oil and grease spills are a safety problem. Granular clay particles are the most effective type of floor absorbent.

Palygorskite and sepiolite are used extensively in agricultural applications as absorbents and carriers for chemicals and pesticides. High heat drying at a temperature high enough to remove the zeolitic water in the structural channels improves the sorbent properties. The chemical or pesticide is mixed with the clay granules and then placed in the ground with the seed. Tests for absorbent granules are done using the General Services Administration's Federal Specification P-A-1056A. The pesticide or chemical fertilizer is slowly released to provide the necessary protection or fertilizer for the growing plant. Finely pulverized clays are also used to absorb chemicals, which can then be dusted or sprayed on the plant or on the surface of the ground.

Another very large use for palygorskites and sepiolites is pet litter. Granular particles of the clay are an effective litter for absorbing animal waste, particularly for domestic cats. The clay granules absorb the waste and greatly minimize the odors.

Haden (1963) described the properties and applications of palygorskite and pointed out both the colloidal and noncolloidal characteristics that make it an important industrial clay. In the past, palygorskite was used as a catalyst in no carbon required (NCR) paper, but today this is a very minor application. An important future application of paygorskite and sepiolite will be in blends with sodium bentonite in landfill and toxic waste liners or barriers (Keith 2000). The estimated annual world production figure in 2004 totaled more than 2,400,000 st. Table 1 gives a breakdown of this estimate.

FUTURE CONSIDERATIONS AND ENVIRONMENTAL ISSUES

All palygorskite and sepiolite are surface mined and, in most countries, the mining company is required by law to reclaim the land. Common practice is to open a cut, mine the clay, and then spoil the overburden from the next cut into the mined-out area. The spoil is leveled or sloped to meet the standards prescribed by the government, and grasses and/or trees are planted. Sometimes the topsoil is put back on top of the spoil and used for agriculture.

In each of the producing areas described in this chapter, the reserves are substantial, so there is no immediate concern about production in the foreseeable future. Current world production is more than 2 Mt. The markets for both palygorskite and sepiolite will continue to expand in the future. An annual growth rate of 2% to 5% is anticipated.

In the processing plants, the major environmental issue is air quality because of dust. Air quality is maintained by using dust collectors on dryers, pulverizers, baggers, and belt-transfer points. These elongate clays have not been shown to be serious health hazards. Dust, however, if inhaled in considerable amounts day after day, can cause lung problems. Therefore, using dust collectors, face masks, and other devices protects the workers from inhaling too much dust. Most clay dust contains quartz, which is a crystalline silica. Crystalline silica is a suspected carcinogen. Most all of the quartz, however, is 20 µm or larger, which is not in the respirable range of 2 to 10 µm. The small amount of quartz in the respirable range is occluded, which means that the quartz is covered by clay particles, so the crystalline silica does not contact the walls of the lungs. Palygorskite and sepiolite contain no deleterious trace elements or chemical compounds that are hazardous to human health.

Several studies have been made to determine if the elongate clay particles are a possible carcinogen, but to date all the results indicate it is not a carcinogen.

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Exhibit 28

MAY -1 2009

Fuller's Earth

Sam M. Pickering Jr. and Fred G. Heivilin

INTRODUCTION

Fuller's earth is a general term for industrially versatile smectite or palygorskite–sepiolite clays (hormites) with high surface area and strong sorptive, binding, gelling, thickening, or decolorizing ability. Fuller's earth has been in common use from perhaps biblical or at least medieval times, when such clays and earths were used for "fulling," or cleaning raw wool to remove greasy lanolin and dirt before the wool was spun, dyed, and woven. The term *fuller's earth*, when used for such a wide variety of industrial clays, has no specific compositional, market, or mineralogical connotation.

Fuller's earths are composed of various combinations of absorptive clay minerals, often with varying amounts of impurities such as silica (at times in the form of fossil diatoms), kaolinite, illite, zeolites, clay-size micas, and carbonate minerals. In general, such clays of marine sedimentary origin in the southeastern United States are commonly called *fuller's earths*, whereas in the American West clays originating by alteration of volcanic ash are typically termed *bentonites*.

Mineralogy, crystallinity, crystal habit and shape, particle size, and crushability are all critical to the sorptive, binding, thickening (gelling), cation exchange capacity (CEC), specific gravity, dusting, deodorizing, and decolorizing abilities of commercial-grade fuller's earth clays. Therefore, these important factors have a profound effect on the refined product's specific industrial uses, market applications, pricing, and customer acceptance.

NOMENCLATURE

Although fuller's earth is a widely used commercial term, it has often been inconsistently applied to a variety of smectites, hormites, bentonites, zeolites, impure diatomites, and other such clay occurrences. The essence of the American Geological Institute's (AGI's) *Dictionary of Geological Terms* definition of fuller's earth is that it is a very fine grained, earthy substance with high water absorptive capacity and ability to refine and decolorize edible oils; it differs from ordinary clay in its higher water percentage and lack of plasticity (AGI 1962). The AGI also applies this term to fuller's earth clays without reference to any particular chemical or mineral composition, texture, or geological origin.

Given that this definition allows considerable overlap that could include many different types and occurrences of other clay materials, more specific fuller's earth definitions may be of interest. Ampian (1985, pp. 158–159) stated that the term fuller's earth "has neither a compositional nor a mineralogical connotation, and the substance is defined as a nonplastic clay, usually high in magnesium, that has adequate decolorizing and purifying properties." Although the term *nonplastic* is often used, it is seldom specified whether it is applied to fuller's earth clays in the raw moist state, after partial drying or in a semicalcined condition.

In the 6th edition of *Industrial Minerals and Rocks,* Elzea and Murray (1994, p. 234) used the term fuller's earth as "more or less a catchall for clay or other fine-grained earthy material suitable for bleaching and absorbent and certain other uses." In a like manner to the AGI usage, they also state that fuller's earths have "no compositional or mineralogical meaning." Elzea and Murray also gave a historical outline of fuller's earth use, which can be summarized as use in antiquity for cleansing and fulling wool; use by the late 1800s for decolorizing and purifying mineral and edible oils; use in the early 1900s for petroleum processing; and use in the last half of the 20th century as an oil absorbent, cat litter, and agricultural chemical carrier granules, replacing petroleum purification as the dominant use. In the mid- to late 1900s, fuller's earths began to be widely used for adsorptive purposes as either natural or acid-activated clays for bleaching mineral or edible oils (Nutting 1943).

Bentonites are similar clays that may overlap with fuller's earths in both commercial application and mineralogy. To simplify the distinction between these two clay types, however, the AGI (1962, p. 49) defined bentonite as "a clay formed from the decomposition of volcanic ash and is largely composed of the clay minerals montmorillonite or beidellite." They specifically restrict the use of the term bentonite to clay that was "produced by decomposition of volcanic ash and not from the decomposition of any other substances." It is interesting that some southeastern fuller's earth clay producers refer to their products used in the foundry sand market as "bentonites," which may serve to obtain a freight-rate advantage over the western bentonite producer's eastern sales.

Some clay researchers explain the origin of many of the southeastern fuller's earth deposits as wind-blown volcanic ash from the west, but they have never been able establish a volcanic source for the presence of hundreds of feet of eastern clay deposits. The present authors (also see Merkl 1989) regard the southeastern smectitic-hormitic clay deposits as having been deposited by normal, nonvolcanic sedimentation in quiet water basins under very low energy in highly saline, anoxic-reducing environments.

Table 1. A historical long-term trend record of U.S. fuller's earth production and average U.S. free on board (f.o.b.) selling prices

U.S. Production*	1940	1950	1960	1970	1980	1990	2000
Short tons, st†	146	395	407	980	1,529	2,541	3,201
Metric tons, t	133	359	370	891	1,390	1,880	2,910
$/st	12.21	26.45	22.55	23.73	49.82	88.00	75.09

Source: Buckingham and Virta 2003.

* Note that U.S. production, unlike statistics from other nations, is of actual refined product tons, not crude clay tons.

† All U.S. domestic sales of bulk fuller's earth product are made by the short ton (2,000 lb).

Table 2. U.S. fuller's earth sales by market use, 2002

Market Application	Sales, st
Pet waste absorbent (cat litter)	1,738,000
Oil and grease absorbents	449,900
Fertilizer pelletizing binder	152,900
Pesticide and herbicide carrier	112,200
Animal feed pelletizing binder	89,700
Filtering, clarifying, and decolorizing	69,630
Fillers, extenders, binders, and drilling mud	64,680
Miscellaneous	290,400
U.S. export	33,990
2002 yearly total sales	3,003,000

Source: Virta 2004.

PRODUCTION

U.S. Geological Survey (USGS) published records (Virta 2004) show that worldwide annual 2002 fuller's earth production was some 3,900,000 t, of which the United States produced and sold approximately 70%. As has been discussed, however, nomenclature of industrial smectite and hormite clays is subject to considerable confusion.

In gathering U.S. and foreign mineral production statistics, the USGS, by policy, does not attempt to precisely identify the type of clay being mined but rather classes each mining company's production based only on what the companies themselves report that they mine (R.L. Virta, personal communication). For several examples, the following instances are rather typical:

- Calcium montmorillonite may be referred to as calcium bentonite in some parts of the United States but is called fuller's earth in England (Harben and Bates 1990).
- In the Florida–Georgia fuller's earth district, near the town of Attapulgus, the clay being mined is informally referred to as attapulgite rather than the mineralogically more accepted term palygorskite. Similarly, palygorskite occurs in two very different crystal habits—as "mountain leather" type material in hydrothermal vein environments and as sorptive gelling clay in anoxic-reducing, semimarine sedimentary deposits.
- Attapulgite (palygorskite) and sepiolite may both be reported by the USGS as fuller's earth production in the United States (Heivilin and Murray 1994).
- Calcium montmorillonite may be referred to by the USGS as "southern bentonite," "Mississippi bentonite," or "Texas Bentonite," although there may be little or no evidence of its volcanic origin.
- Large tonnages of sorptive clays produced for cat litter products in Spain and Senegal are variously referred to as sepiolite, meerschaum, and attapulgite in the same publication (Newnan 2003) and as both fuller's earth and attapulgite (Virta 2004).

U.S. fuller's earth production tonnage and product prices (exclusive of bentonites) have grown with the national economy over the past 70 years, as reported by Buckingham and Virta (2003) in thousands of tons and average selling price in Table 1.

The USGS (Virta 2004) lists U.S. production of processed fuller's earth products for 2002 as 3,003,000 st (2,730,000 t), which sold for $246 million (or an average 2002 price of $81.92 per processed short ton). This total production was from 12 listed states: 5 companies in Georgia; 3 companies each in Florida, Mississippi, and Nevada; 2 each in California and Virginia; and a single company each in Kansas, Illinois, Missouri, Oregon, Tennessee, and Texas. Additionally, the USGS (Virta 2004) reported U.S. 2002 total fuller's earth sales by generalized market application (Table 2).

Fuller's earth is such a versatile industrial minerals material that many of its commercial uses do not fit conveniently into such simple categories, so this listing should be regarded as reflecting only generalized market segments. Also, by law the USGS is required to avoid listing production statistics for mineral market uses served by only one or two producers because that would divulge confidential production and sales information. This practice has the effect of putting much of specialized production into the miscellaneous category. Similarly, the USGS (Virta 2004) reports estimated 2002 world fuller's earth production from market economy countries (France, India, Iran, Japan, and Turkey unreported; Table 3).

HISTORICAL U.S. PRODUCTION AND PATTERNS OF USE

Native Americans were reported to have used fuller's earth and bentonite for cleaning blankets and clothing before European arrival in the 15th century. During the Revolutionary War, soldiers stationed near Perth Amboy in New Jersey used Woodbridge fire clay to clean their buckskin clothing. In the early 1800s, fuller's earth was discovered in association with an iron ore bed near Kent, Connecticut. During the Civil War, fuller's earth was used to bleach sugar near Falls City, Texas.

The first documented commercial fuller's earth deposit in the United States, which is still being mined today, was discovered in 1893 near Quincy, Florida. The Owl Commercial Co. (predecessor of the present makers of White Owl cigars) made the discovery during their attempt to make burnt brick from clays on their Quincy tobacco plantations. Because of its high content of smectite, the clay was unsuitable for brickmaking. One of the Alsatian farm workers in the area, however, recognized the Quincy clay as similar to fuller's earth, which was being mined in Germany. Two years later, his observation led to development of the first U.S. mine for fuller's earth for processing mineral oils. Also, fuller's earth had been mined slightly earlier on a small scale in Arkansas in 1891 (Miser 1913) and tested for use in refining cottonseed oil.

The U.S. demand for acid-activated fuller's earth for edible oil and petroleum refining and decolorizing expanded rapidly until it peaked at about 317,000 st in 1930. At that time, this was about 90% of total U.S. fuller's earth production. After 1930, the use of fuller's earth for petroleum refining decreased because of the availability of alternative oil refining methods.

After that time, U.S. oil refining use of fuller's earth declined until it reached a uniform rate of 35,000 to 40,000 stpy for edible oils only. Using fuller's earth as a waste oil absorbent and floor-sweep type of clean-up agent, however, began before World War II and, by the 1950s, its use as a carrier for herbicides and pesticides had become more prominent. Cat litter production began in 1952, and it has grown rapidly since then.

In the district between Quincy, Florida, and Attapulgus, Georgia, the excellent gelling properties of palygorskite (attapulgite) fuller's earth were discovered and developed for salt water drilling mud, as a joint binder taping compound for sealing the seams of construction wallboard, and for other applications requiring a thickened gelling clay. These uses for gelling fuller's earth products developed to replace sales lost when use for petroleum refining declined. The Florida–Georgia mining district today is the world center for gelling fuller's earth clay production.

What is now by far the most prominent American use for fuller's earth, as a pet waste absorbent product (cat litter), began to grow rapidly in the 1950s. At first, cat litter was made from oil absorbent product that had been crushed to finer than 3/4-in. size, semicalcined in countercurrent rotary kilns, milled and screened, and packaged for retail sale. Today, cat litter is typically dried to only 4% to 15% moisture, which results in improved absorption, reduced dusting, and lower energy cost.

In the early 1990s, clumping cat litter became very popular. Blending western bentonite or clumping agents with eastern fuller's earth causes liquid waste to form clumps that can easily and neatly be taken from the litter box with a perforated scoop. This leaves only unused clean granules in the litter box, minimizing waste and enabling easy handling of a formerly messy and unsanitary chore. Today, many clumping cat litter products are up to 100% western sodium bentonites.

GEOLOGY

Mineralogy

Typically, fuller's earth is a marine or semimarine sedimentary clay variably composed of the clay mineral groups smectite and hormite. Tables 4 and 5 summarize these closely similar types of clay minerals.

In 1862, Savchenkov first used the term *palygorskite* to define a vein-type hydrothermal "mountain leather" clay mineral from the Palygorsk locality in the Ural Mountains of Russia (Hey 1975), where it was mistaken at first for a variety of asbestos.

J. de Lapparent first termed the highly absorptive gelling clays from Decatur County, Georgia (United States), and also those from an area near Mormoiron, France, with the mineral name *attapulgite*, because he thought those clays quite different from palygorskite. The new name was applied to gelling clays occurring near the small southern Georgia town of Attapulgus. More recently, however, x-ray diffraction proved the two clay types to be the same mineral (Bailey et al. 1971). Although first applied later than palygorskite, the name attapulgite is still in common informal use in the Florida–Georgia mining district where the crystal length-to-diameter ratio does not exceed 10:1 (Merkl 1989).

In 1774, Glocker first applied the name *sepiolite* for a clay mineral later called "meerschaum" by Werner in 1788. Hauy in 1801 described the same type of low-density white magnesium silicate clays as *ecuame de mer*, which Brochant in 1802 also termed *talcum plasticum*. Today, this type of magnesian clay mineral is known as sepiolite and is found more abundantly in the northern extent of the Florida–Georgia basin than more southerly concentrations of attapulgite near Quincy.

Table 3. World production of fuller's earth, 2002

Producing Nation*	Production, t
Algeria	3,521
Argentina, estimated	1,500
Australia, attapulgite	6,000
Germany (unprocessed)†	500,000
Italy	30,000
Mexico	150,000
Morocco, smectite	42,243
Pakistan	15,000
Senegal, attapulgite	176,454
South Africa, attapulgite	7,900
Spain, attapulgite, estimated	90,000
United Kingdom, estimated product	140,000
United States	2,730,000
Rounded world total	3,890,000

Source: Virta 2004.

* Excludes centrally planned economy countries.

† Crude rather than processed product tons of clay.

Table 4. Smectite group minerals

End-Member Mineral	Crystal System	Chemical Composition
Montmorillanite	Monoclinic	$(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}\bullet nH_2O$
Beidellite	Monoclinic	$(Na,Ca_{0.05})_{0.33}Al(Al,Si,)_4O_{10}(OH)_2\bullet nH2O$
Nontronite	Monoclinic	$Na_{0.33}Fe_2(Si,Al)_{10}(OH)_2\bullet nH_2O$
Hectorite	Monoclinic	$Na_{0.33}(Mg,Li)_3Si_4O_{10}(F,OH)_2$
Saponite	Monoclinic	$(Ca/2,Na)_{0.33}(Mg,Fe)_3(Si,Al)_4O_{10}\bullet 4H_2O$

Source: Roberts, Campbell, and Rapp 1990.

Table 5. Hormite group minerals

End-Member Mineral	Crystal System	Chemical Composition
Palygorskite*	Orthorhombic and monoclinic	$(Mg,Al)_2Si_4O_{10}(OH)\bullet 4H_2O$
Sepiolite	Orthorhombic	$Mg_4Si_6O_{15}(OH)2\bullet H_2O$

Source: Roberts, Campbell, and Rapp 1990.

* Informally termed attapulgite in the Florida–Georgia, Spain, and Senegal mining districts.

The reader is referred to the Bentonite, and Palygorskite and Sepiolite chapters of this book for a more detailed discussion of the mineralogy of the smectite group and hormite minerals, respectively.

Origin

Fuller's earth clay deposits in the eastern United States are found in marginal marine sedimentary units that formed in restricted, anoxic, shallow, low-energy, reducing, and often hypersaline conditions. Such depositional environments favor formation of magnesian montmorillonite, palygorskite (attapulgite), or sepiolite.

Alternatively, sorptive calcium montmorillonite fuller's earth deposits have been formed in Nevada in Pliocene freshwater lakes with as much as 40% siliceous diatom tests. In south-central

California, what is now the Miocene Antelope Shale was originally deposited as diatomite and then diagenetically altered by deep burial to a form of absorbent opal CT.

Other inert, nonabsorptive, accessory minerals in fuller's earths can include dolomite, calcite, quartz (sand, silt, biogenic opaline CT, or diatomite), gypsum, and assorted heavy minerals. Finely divided fossil organic plant matter can color the fuller's earth gray or bluish gray; oxidative weathering alters the clay to a cream, tan, green, pink, or yellowish tint.

Physical Properties

Mineralogy of fuller's earths determines their most effective potential use. Monmorillonite is a type of clay mineral that shrinks when dried and may swell when rewetted. Highly adsorptive when dried, this mineral is used in granular animal litter, in floor-sweeping compounds, and as a carrier for insecticides, herbicides, and so forth.

The extremely fine particle size, high CEC, and tight packing of attapulgite- and montmorillonite-rich fuller's earths make them useful to increase "stickiness" and promote high green strength in ceramic dinnerware; to provide adhesion and plasticity in metal foundry molding sands; as an adhesive binder to form pellets of taconite iron ore, agricultural fertilizers, and so forth; and to form an impermeable seal or slurry barrier for isolation of sanitary landfills and hazardous waste disposal sites.

Bleaching clays with or without acid activation need a particular pore size and porosity to clean and decolorize edible oils. There are only two such actively mined fuller's earth clay deposits in the United States—in northeastern Mississippi where acid activation (the clay slurried with acid) is necessary and in the south Georgia district near Meigs, where clays bleach naturally or with only acid addition to the dry powdered product.

The presence of attapulgite in elongate needle-shaped or acicular habit crystals is indicative of superior gelling or thixotropic behavior when slurried with water or liquid polymers. Such fuller's earths can be used for oil-field drilling muds, which retain their integrity as thick and viscous gels, even in the presence of saline formation brines. Magnesian fuller's earths can also be used in thickened or gelling form to produce nondripping paint, to thicken liquid detergents, for wallboard joint cement and spackle compounds, and for other specialty applications.

In the Florida–Georgia fuller's earth mining district, attapulgite commonly occurs in two distinct forms known as short- and long-length crystalline material. The higher gelling long-length clays are found in the southern part of the district and are stratigraphically restricted to the Mid-Miocene age Dogtown Member of the Hawthorn Formation of northwestern Florida. Dogtown attapulgites are typically longer in crystal habit than 10 µm and are associated with the most favorable gel-strength clays. The slightly younger Meigs Member clays contain short attapulgite crystals less than 10 µm long and are more prevalent in the northern portion of the fuller's earth mining district in southeastern Georgia near Ochlocknee.

Sepiolite clay also occurs in needle-like crystal habit in the more northerly Meigs Member and remains stable at relatively higher temperatures. Thus sepiolite-rich fuller's earth products can be useful as drilling muds for maintaining borehole circulation when completing geothermal production wells.

DISTRIBUTION OF MAJOR U.S. DEPOSITS

Southeastern United States

Fuller's earth deposits of commercial quality and accessible for shallow open-pit mining are mostly found in several districts in the southeastern United States, where relatively low-energy, warm, restricted coastal marine conditions were prevalent during late Mesozoic and Cenozoic times.

These southeastern fuller's earths are found in three main stratigraphic formations:

1. In the Mid-Miocene Dogtown and Meigs members of the Hawthorn Formation in the mining district between the towns of Quincy, Havana, and Dogtown in the panhandle of north Florida, and Attapulgus, Reno, Calvary, Cairo, Ochlocknee, and Meigs in southwestern Georgia
2. In the Late Eocene Twiggs Clay Member of the Barnwell Formation in the area east of Wrens in Jefferson County, Georgia
3. In the Late Paleocene Porters Creek Clay between Cairo and Mounds in Pulaski County at the southern tip of Illinois, and in the towns of Ripley and Blue Mountain in Tippah County, Mississippi

The Florida–Georgia District

A narrow depositional trough trends southwest to northeast across the Florida Panhandle region from the town of Quincy to near the Georgia towns of Attapulgus, Meigs, and Ochlocknee (Herrick and Vorhis 1963). This restricted basin, variously termed the Gulf Trough or the Apalachicola Embayment, has localized fuller's earth deposits in the Miocene-age Hawthorn Formation that dominate U.S. production of both granular and gelling-grade industrial clays.

Suggestions have been made that fuller's earth clays in the Florida–Georgia District originated from altered volcanic ash (such as in Reynolds 1970); more recent research (Thomas 1981), however, has shown no indication that these marine and semimarine clays were deposited in any conditions other than normal, nonvolcanic, reducing environments in shallow sedimentary basins.

Gelling-grade magnesian attapulgite (Figure 1) is much more concentrated in the Dogtown Member of the Hawthorn Formation at the narrowest southern end of this trough or basin; and the smaller percentages of sepiolite and shorter-crystal-length attapulgite- and montmorillonite-mixed clays of the Meigs Member are more abundant toward the northern end. The Florida–Georgia area underlain by this Miocene-age trough has been continuously and extensively mined for various grades of fuller's earth for more than a century.

This depositional trough is thought to have begun as a considerably older graben structure that served as a major ocean current seaway throughout much of the early and mid-Tertiary but was broadly uplifted in the Miocene when much of what is now Florida was raised by the Peninsular Arch (Herrick and Vorhis 1963; Huddlestun 1993). During the mid-Miocene, the trough was uplifted and cut off from open ocean circulation; it became a series of discontinuous, small to extensive, evaporitic basins rich in magnesian salts, where dolomitic limestone, attapulgite/palygorskite, and sepiolite were deposited.

The Virginia District

Two fuller's earth producers in east-central Virginia mine a rather heavy, marginal-grade diatomaceous mudstone for cat litter in the Miocene Calvert Formation (Hosterman and Patterson 1992). This material, although not of superior quality, has a considerable freight advantage in shipping to the population centers in northeastern cities.

The Mississippi Embayment District

A wide Coastal Plain sedimentary embayment or open-fronted basin extends inland along the course of the Mississippi River as far north as Cairo and Mounds, Illinois. This continuous outcrop belt of the Late Paleocene-age Porters Creek Formation from Ripley and Blue Mountain, Mississippi, to Mounds and Cairo contains many fuller's earth deposits that are as much as 370 ft thick.

These Paleocene-age calcium montmorillonite clays have less desirable higher-density and lower-absorbency characteristics than clays from the Florida–Georgia district. Their freight advantage to the large midcontinent market area, however, and their ability to blend with western swelling bentonite to provide good liquid-clumping capacity allow their extensive use in the cat litter trade. Some companies blend the weathered light-colored clays with darker, unoxidized clays to produce an attractive "salt and pepper" colored product from the Porters Creek clay district.

The U.S. Western District

Different types of fuller's earth are produced in the western United States, such as at California's San Joaquin Valley, where absorptive mixtures of opal-CT altered from diatomite are present. Two high-grade fuller's earth deposits in Nevada, composed of mixed montmorillonite and diatomite, have been proven for quality and passed standard validity exams for granular cat litter and oil absorbent, but they have not yet been brought to the market. Some sepiolite gelling clay is found in east-central California, but it is of marginal quality and sold mainly in the West Coast market.

EXPLORATION METHOD

Fuller's earth exposed in surficial outcrops is commonly too weathered and oxidized by soil-forming processes to have sufficient quality for industrial use. New fuller's earth deposits are often discovered by widely spaced core drilling near areas where the clay was mined or near outcrop exposures that look promising.

Truck-mounted rotary drilling rigs of the type developed for placing explosive charges for early oil-field geophysical exploration—such as the 500 and 1250 models built by Failing, Gardner-Denver/Mayhew, and DSM—are used for the drilling depth of 100 to 200 ft common in fuller's earth exploration. Double-tube core barrels with built-up hard metal bits are used, and the core is extruded with water pressure from the drill rig's mud pump or with compressed air. Typically, NX-size core of about 2⅛-in. diameter is recovered; rinsed and trimmed; marked accurately by property code number, hole grid location, and depth in the hole; and transported in boxes or bags to the company laboratory for extensive quality testing.

When an area of core holes tests favorably in the laboratory, accurately spaced core-drilling campaigns are begun on a surveyed grid of 400 to 800 ft. As the shape, extent, and quality of new clay deposits are proven, grid drilling is narrowed to spacings of 200 and 100 ft before overburden stripping is begun.

After the commercial clay surface is exposed, closer spaced drilling may be done using air-pneumatic or auger methods, or the area may be sampled with a mining backhoe. Regulated wetlands, endangered species areas, and archaeological sites are avoided wherever possible. Lately, however, mitigation is needed for wetland areas that must be crossed by haul roads or those underlain by high-quality fuller's earth that the company wishes to mine.

Fuller's earth quality is posted from drill and laboratory testing results on carefully scaled grid maps, which are used for mine planning, government permitting, and future clay reserve tonnage calculations. These mine planning maps show overburden thickness and type, clay thickness and commercial quality, location of property boundaries, and regulated wetland areas.

Figure 1. Foliate texture of high-magnesian attapulgite gelling-grade fuller's earth from the Florida–Georgia District near the axis of the Gulf Trough depositional embayment. This texture develops shortly after the raw clay is exposed for mining and is thought to be an indicator of high gelling strength. (Knife, for scale, is 10 cm long.)

CLAY QUALITY CHARACTERISTICS

Special Characteristics

The fuller's earth industry, particularly perhaps in North America, has become accustomed to applying special terms to different properties of clays and their products. These terms may not be familiar to those outside the industry, so some simplified explanations may be helpful, as follows:

- *Clumping clays* are those clays with clumping agents or a high content of western sodium bentonite; they have become very popular for clumping or scoopable-type cat litter products. The bentonite absorbs liquid wastes, which clump in discrete lumps that can be neatly scooped from the litter box, leaving only clean litter behind. Bactericides are needed to improve long-term odor reduction in western bentonite clumping cat litters.
- *Dusting clays* are those clays that are unsuitable for granular products because they break down too finely upon crushing or during shipping, handling, or use. In cat litters, a high dusting clay product causes mudding, tracking outside the litter box, and a dirty cat.
- *Heavy* or *high-density clays* is a term used for cat litter products that are denser than about 40 lb/ft^3. These products typically are lacking in absorption, take up more room in the cat

box, are inconvenient for the retail purchaser to carry, and commonly do not control odors as well as lighter clays.

- *Gelling clays* is a term used for clays that have a high slurry viscosity at low percent solids; these clays are used as a thickening agent for wallboard-tape joint cement, nondripping paints, drilling muds (especially palygorskite, used to maintain circulation when drilling in brine formations), and liquid detergents, and as a fine pulp retention aid in paper manufacture, liquid fertilizer suspensions, adhesives and sealants, putties and glazing compounds, and other industrial applications. Gelling viscosity is typically measured on Fann or Brookfield viscometers. Gelling behavior and viscosity can be enhanced by extruding the moist clay to align the needle-shaped crystallites or by adding calcined magnesium oxide.
- *Granular clays* refers to products that are carefully crushed and screened to a narrow range of chip sizes, often listed such as "4–20" (passing through a U.S. Standard 4-mesh screen and retained on 20 mesh). The granule size controls product surface area and liquid or gas absorption in the animal litter.
- *Slaking clays* are those clays that, after drying, break down to mud when wetted with water or oils. Slaking is a very undesirable quality in granular fuller's earth products because it decreases odor control and increases liquid buildup in cat litter and causes unsafe slippery conditions when used as a floor-sweep compound type of oil absorbent product. Slaking is caused by dispersion of the surface of the clay granules to form a slick surface, in which the clay crystallites are uniformly negatively charged and consequently repel each other. Paradoxically, although slaking is undesirable behavior in granular fuller's earth products, it is essential in gelling clays.

Quality Testing

Companies that produce fuller's earth test their exploratory drill core and quality control samples against a variety of published and unpublished product specifications that are important to their customers. Fuller's earth product specifications are set by the type of market use intended. The initial critical quality factor is the percentage of coarse inert impurity materials, commonly termed *grit,* that contaminate the clay deposit. Grit specifications for the maximum allowable nonabsorptive minerals present in crude clays can range from 5% to as much as 15%. Some of the coarser grit material can be partly removed by air separation at the whizzer during dry milling or by oversize screening when producing granular products.

Dry calcined MgO can be added to the raw clay during processing to improve gelling, viscosity, and thickening behavior. It may be necessary to extrude the moist clay for crystallite alignment or to allow for a seasoning time of up to 2 weeks to allow the MgO to have its maximum desired effect.

Granular fuller's earth products commonly must be composed of a narrow size range of chip particles, with very little fine dust-size material allowed. Dusting behavior can be a problem with many of the softer or more frangible absorbent fuller's earth products. When dried or semicalcined and then crushed to a granular or chip-sized product, the finer mesh sizes of clay may need to be removed and discarded to meet the customer's particle-size specifications. De-dusting boxes and liquid polytetrafluoroethylene addition may be used to reduce airborne dust immediately before packaging. Slaking is also a quality problem, where the clay granules break down when wetted and form an impermeable, nonabsorbent muddy mass.

The American Petroleum Institute (Anon. 1969) lists drilling mud specifications. Specification P-A-1056A, published by the U.S. General Services Administration, describes tests for floor-sweep-type absorbent granules. The American Oil Chemists' Society (Anon. 1958) describes edible oil bleaching tests. Weidhaus and Brann (1955) describe testing for the various types of insecticide, carrier, and dusting diluents.

Product Performance Standards

The following are general guidelines for specific fuller's earth products intended for particular market applications.

Granular products intended for cat litter should be light in color with a loose packaged density of less than 50 lb/ft^3, and when crushed they should produce a minimum of fine dust-size material. Low bulk density is especially important for high-quality consumer cat litter; the purchaser will select generous-size packages that weigh as little as possible.

The same low bulk density, however, will increase per-ton shipping cost in railcars and export containers. Litter granule size usually ranges from about 4 to 30 Tyler screen mesh, and liquid absorptivity ranges from 50% to 120% without slaking or granule breakdown. Cat litter products are typically dried to 10% to 15% moisture, and western bentonite is commonly added to absorb liquid waste into easily removed, scoopable clumps.

Granular oil-absorbent fuller's earth products vary in density from 22 to 52 lb/ft^3, with nonslaking oil absorption ranging from 50% to 100%. Hard granules, low dusting, and high adsorption ability all bring a premium price for this type of product, which is generally sold at 0% moisture.

Agricultural granules for use as carrier agents for liquid insecticides, herbicides, bactericides, nutrients, and fungicides are generally sold in screen sizes ranging from 24 to 48, or 30 to 60 Tyler mesh, with minimal dusting or slaking allowed. These products are commonly produced from Porters Creek Clay in the midcontinent Mississippi Embayment area and are dried to 0% moisture.

Gelling-type fuller's earth products are tested by measurement of slurry viscosity at low clay solids percentages. The most widely used viscometers are the low shear Brookfield unit at 100 rpm or the high shear Fann unit at 600 rpm, depending on customer preference and market application. Clay slurry viscosity can be tested with either fresh or supersaturated saline water.

Magnesium-rich attapulgite fuller's earth clays retain good gel strength under saline conditions, whereas sodium- or calcium-based montmorillonite gelling products break down in the presence of salt water. Therefore, attapulgite fuller's earth is selected as a high-gelling drilling mud for oil and gas exploration when expecting saline formation conditions. For such drilling use, a 600-rpm clay testing 30 Fann units will equate to 100-bbl yield units of properly thickened mud per ton.

Bleaching fuller's earth clays are used to purify and remove discoloring agents from edible oils and liquid products. These products must have very specific pore sizes and shapes to absorb impurities properly while allowing the clarified liquid to filter easily through the clay. The only U.S. fuller's earth products suitable for this use are produced in the Jackson Area of Mississippi and the Meigs to Ochlocknee mining districts of Georgia. These specialty clays are dried to no less than 10% moisture, ground to finer than 325 mesh, and acid treated or soaked for enhanced activation.

Fuller's earth used for sports turf or lawn growth aids (for athletic playing fields or golf courses) is usually dried hard at high temperature to light red, making granular products similar in size to cat litter. These products loosen soils for better drainage and more effective use of plant nutrients.

MINING

Fuller's earth is mined by open-pit methods (Figure 2). Generally, mine planning and permitting, followed by overburden excavation, are based on core drilling on grids of 50 to 100 ft and careful clay quality testing. Overburden is, whenever possible, backfilled into nearby previously mined-out pits and sloped to blend in with the original, premining terrain. After the overburden is removed, closer spaced drilling using compressed air or auger sample return is frequently done on 50 to 25 ft spacing for effective mine quality control.

Overburden is stripped with backhoe excavators and off-road haul trucks, or dozers and scrapers, often by local independent contractors (Figure 3). The clay itself is excavated with backhoes, front-end loaders, or scrapers. Because sedimentary fuller's earth was deposited in horizontal layers or strata, quality control is much more reliable if the clay is mixed during mining by vertical excavation (such as with hydraulic backhoes). This vertical mining averages out the horizontal layering of quality variations and delivers better-blended crude clay to the stockpile or processing plant. Acceptable overburden thickness can range from only a few feet or meters to more than 100 ft, depending on the mining district, ore zone thickness, clay quality, and the market value of products produced.

Highway haul trucks transport the crude clay from the property; they must meet complex state and interstate regulations for haul weight, individual wheel load bearing, spillage, tracking mud onto the paved road surface, and so forth. Thus, there is a real cost and efficiency advantage to mining near enough to the clay processing plant so that mine-run crude clay can be hauled by very large off-road trucks on privately owned roads, where regulated load limits do not apply. After a fuller's earth plant has operated for a few decades, however, it is likely that most or all of the nearby acceptable quality clay deposits have already been mined out.

Mine Permitting and Regulation

Proposed fuller's earth mines must be approved and permitted by state and local agencies. Each mine permit process addresses reclamation, air quality, stormwater runoff, local zoning, and other regulatory issues. The permit process can be very different from state to state, and may vary considerably through time in an individual state. Careful attention should also be paid to wetlands, county zoning regulations, Native American tribal customs and practices, proximity to historic homes or buildings, parks, natural areas, wildlife sanctuaries, or endangered species regulations.

Mine permitting must also deal with land and mineral ownership and leasehold rights, mine water control, highwall slope stability (typically laid back to between 0.5:1 and 2:1 angles), adjacent property setback, and so forth. Mineral rights on privately owned lands are commonly leased from the landowners, and royalties for extracted clay are paid by the ton or cubic yard.

Failing to obtain a satisfactory lease contract, mining companies may purchase clay properties outright or buy the deeded, severed minerals only and leave surface and timber ownership to the landowner. On federal lands, the U.S. Bureau of Land Management or the U.S. Bureau of Indian Affairs must handle mineral leasing or placer claims in accordance with the General Mining Act of 1872 and their own particular standards and regulations.

Mined Land Reclamation

Once mining is completed, the mined-out pits are backfilled and leveled with overburden from a nearby or adjacent cut, or developed into fishing ponds. The disturbed land is restored to attractive, stable, noneroding, less than 3:1 slopes. Cover crops of pasture grass and select tree seedlings are planted on the reclaimed land to leave little or no hint that the property had ever been mined. Individual states, and in some cases also a county or smaller local permitting agency, control regulation of such privately owned disturbed mining lands in the United States.

Figure 2. Typical open pit fuller's earth mine near Ochlocknee, Georgia, showing the excavated surface of the minable clay under approximately 20 m of overburden. Ore zone thickness is approximately 4 m.

Figure 3. Mining fuller's earth clay after overburden has been removed and hauling by highway truck to the processing plant. Note overburden in the background that has been backfilled to fill the previously mined-out pit.

CLAY PRODUCT PROCESSING

Fuller's earth is an unusually versatile mineral that can be processed to meet a rather bewildering variety of product specifications for sales to a wide range of differing market uses. Crude run-of-mine fuller's earth is typically crushed and semidried with a shredder or hammer mill, Raymond mill, Williams mill, or Imp mill for bleaching and gelling products.

The clay may be dried to 10% to 15% moisture or semicalcined. Care is taken not to overheat and reduce pore size, absorption, or CEC, and alter mineralogy to make cat litter, bleaching and oil-adsorbent material, agricultural chemical carriers (for pesticides, herbicides, etc.), jet fuel filtration agents, or turf improvement products.

Various-sized granular products can be screened to make any product from 4 by 12 mesh, 30 by 60 mesh, or even as fine as 60 to 90 Tyler mesh specifications. Finer clay products can be ground and air-float separated to finer than 200 mesh, 325 mesh, or even ultrafine –6-µm material. The moist clay can be "pugged" (extruded) to align elongate crystals and improve gelling properties.

MgO may be added to improve product viscosity and gelling characteristics. There is not agreement in the industry on whether adding MgO causes actual attapulgite crystal needle growth after a few days' residence in the clay product, or if the MgO simply results in an improved surface charge on the existing clay crystallites that results in better gel performance.

PRODUCT HEALTH AND SAFETY CONSIDERATIONS

Crude fuller's earth clay is checked by scanning electron microscope, transmission electron microscope, x-ray diffraction, and x-ray fluorescence chemical analysis for the presence of industrial fibers of possible asbestiform characteristics, cristobalite, trace metals, and other possible hazardous elements. Because some fuller's earth products may be used for processing animal and human foods, all products and additives used must meet food-grade standards. Several examples of possible hazardous situations that have affected fuller's earth operations are as follows:

- Development of East Gate, Nevada, mordenite for cat litter use was halted because of the presence of erionite fibers in the crude clay and overburden.
- Use of fuller's earth cat litter in California was challenged because of the presence of crystalline silica. It was necessary to obtain a "Safe Use Determination" by the Sorptive Minerals Institute to enable the sale of most types of cat litter in the state.
- The National Institute for Occupational Safety and Health (NIOSH) conducted a health study to ensure that the type of elongate crystals in palygorskite in the Florida–Georgia fuller's earth district did not constitute an asbestiform mineral health hazard.

PRODUCT PACKAGING, TRANSPORT, AND MARKETING

Finished granular fuller's earth products such as cat litter, oil absorbents, and floor-sweep compounds are sold in consumer-attractive paper or plastic packages of 5 to 50 lb or in metric sizes for export markets. Cat litter packaging has evolved from unweighed filling of semicalcined clay into hand-stapled bags in 1952 to fully automated bag-filling units that shrink-wrap bundles which are then conveyed onto automatically stretch-wrapped pallets for warehousing and then loading onto trucks or railcars.

Agricultural chemical carriers, jet fuel filtration products, bleaching clay granules, anticaking or dry-flow agent clay powders, specialized drilling muds, and gelling or thickening agents are shipped in 40- or 50-lb paper bags, polypropylene bulk big-bags, bulk truckloads, or railcars.

Some export fuller's earth products are shipped overseas in large metal shipping containers, covered barges, or bulk ship holds. Although the industry packaging trend is toward nearly complete automation, some fuller's earth products continue to be hand-bagged and -palletized.

Finished fuller's earth products may be distributed to a market radius of only a few hundred miles for typical high-density, low-absorption cat litter or to worldwide markets for high-grade bleaching clays. Order size can range from barge load or shipping cargo bays, or 80- to 120-truckload special promotions, to individual pickup truck loads destined for the local hardware store. Generally, the main tonnage of fuller's earth products is shipped to market in truckloads, railcars, or in metal shipping containers.

Individual fuller's earth customers can be hardware stores, municipal or hazardous waste landfills, city or university athletic fields for turf enhancement granules, jet fuel purification facilities at major airports, or multibillion-dollar distributors for chemical, grocery, or discount consumer sales outlets.

Product sales go through regional or national distributors or directly to the wholesale or retail customer. Fuller's earth products are sold in the neighborhood grocery store in attractive small packages for household cat litter or to a paint manufacturer for use as a thickener and antidrip agent.

The overall trend in the fuller's earth industry is to develop new products that better satisfy the particular customer's needs and allow a higher added-value price over standard or commodity grades. New product development research must consider fuller's earth mineralogy, physical and chemical specifications, existing patent rights, customer service and packaging preferences, and extra processing and energy cost requirements before launching innovative higher-value products.

The future of the U.S. fuller's earth industry depends on developing and patenting new special-use products and reaching new types of market applications.

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Exhibit 29

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ATTAPULGITE--THE RELATIONSHIP BETWEEN ITS PHYSICAL/ CHEMICAL PROPERTIES AND CURRENT COMMERCIAL APPLICATIONS

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Zile -
gel clay -
general -
applications

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Abstract. Attapulgite is a magnesium aluminosilicate clay mineral which exhibits unique, processing-enhanceable physical and chemical properties that are related to its current commercial uses. Properties of commercial interest are gelling, absorption, adsorption, binding, acid neutralization and many others. Major industrial applications are: (1) absorption by heat treated grades utilized in industrial oil and grease absorbents and in agricultural pesticide carriers; (2) gelling of aqueous liquid products by colloidal grades for stabilization and viscosity control in salt water drilling fluids, suspension fertilizers, liquid animal feed supplements, paints and tape joint compounds; (3) adsorption by heat treated varieties for the removal of catalysts, color bodies and other polar compounds from hydrocarbon streams; (4) gelling of organic liquids by colloidal attapulgite/surfactant blends in oil-type paints, fibrated and nonfibrated asphaltic coatings and mastic compositions, and (5) the binding of feeds and molecular sieve sorpents with colloidal type attapulgite products. These applications and other less common uses and potential uses will be discussed along with the necessary selective mining and plant processing features related to each property and application.

Introduction

Attapulgite is the principal mineral of attapulgus clay. Attapulgite is a unique hydrated magnesium aluminum silicate. Co-occurring minerals are montmorillonites, calcite, dolomite, quartz, feldspars and, rarely, sepiolite (Grim, 1968). Often the clay as mined contains organic materials such as roots and bark plus the leached microbial decay products from forest floor humus. The morphology and structure of attapulgite has been described well by many (Grim, 1968; Haden and Schwindt, 1967). Briefly, attapulgite is an acicular magnesium aluminum silicate with dimensions of 1 to 2 micrometers in length and a width of 0.01 micrometers. The needles are honeycombed with channels. The structure (Bradley, 1940) consists of a double chain of silicon-oxygen tetrahedrons running along the long axis that are blocked apart by discontinuous units of Mg in sixfold coordination to form the channels. Al, Fe and other elements partially replace Mg in the actual composition. The water content and the positions of the water molecules (or OH groups) in the crystal are of utmost importance in the thermal processing of attapulgite during plant preparation to achieve desired properties in various types of finished attapulgite clay products. Types of water encountered are free moisture (FM) which is moisture present in excess of the zeolitic water; crystal water coordinated to certain magnesiums in the clay, zeolitic water held in channels and hydroxyl water that can be driven off at higher temperatures. During the plant thermal processing of the clay water removal is a function of temperature and time. In a DTA analysis the sequence of events observed has been: (1) FM water was driven off at 100°C, (2) zeolitic water was driven off between 100-200°C, (3) at higher temperatures crystalline and OH water were removed (Haden and Schwint, 1967). In commercial products this sequence is complicated by the normally present calcite contaminant ($CaCO_3$), or the less frequently encountered dolomite contaminant ($MgCO_3 \cdot CaCO_3$) since the CO_2 from the $MgCO_3$ portion of dolomite is evolved at the same temperatures as the OH water while the CO_2 from $CaCO_3$ is driven off at higher temperatures, >1200°F (649°C).

The surface areas of commercial attapulgites range from 220 m^2g to 120 m^2/g with the higher surface areas being noted for colloidal, gelling grade products and the lower surface areas for the higher temperature, thermally-processed products. The surface areas cited are for N_2 gas using the B.E.T. techniques. The channels are involved in the B.E.T. surface area measurement. This is a large surface area and is related to the use of attapulgite as an adsorbent in purification, although the channels are not normally involved in these phenomena. Other notable surface characteristics are medium to strong acid sites and oxidative sites. The surface also is a source of alkaline materials since attapulgite water slurries generally exhibit pH values of 8.5 to 9.5.

Mining, Processing and Commercial Applications

General

Fields of commercial use of attapulgite are based on its properties as shown in Table 1. Briefly the properties utilized are water gelling, bulk absorption of liquids, surface adsorption, and miscellaneous. The miscellaneous properties are the clay's ability to hold and release water up to fairly high temperatures; to bind materials and stick them together while leaving an open structure, the characteristic of interacting with or neutralizing acids, toxins and certain leuco dyes; and to be dispersed in and gel organic liquids when specified surfactants are used in conjunction with the clay. As would be anticipated, there are many different clay products involved in this multiplicity of uses. Desired properties are achieved by selective mining and by various plant processing treatments.

Selective Mining: Practiced by all American attapulgite product producers. It consists of the testing of precored, cleared mine site samples and face sampling open seams so that the samples can be classified for certain end uses. Sample evaluations consist of the lab preparation of small amounts of plant-type products which are then evaluated with suitable tests to determine such properties of gelling, rate of viscosity development, absorption, adsorption, etc. As a result of this lab testing, mining is carried out on selected strata in well defined areas, the crude is labeled, shipped in to the processing plant and segregated into various storage areas. Each area has classified crude piles which can be blended to provide a mix which will give desired properties after processing to a final product. For example, the gelling grade crudes are separated into those which give low, medium and high viscosity gelling products. These are blended, based on availability, to give a final gelling grade product with uniform viscosity-building properties. Similar practices are utilized to provide final products that will show uniform properties in other applications.

Plant Processing: Has a profound effect on the properties of the final products made. For example, excessively high processing temperatures irreversibly ruin gel building properties, slaking properties in water and, if very high, the sorptivity of the clay. The degree of grinding has an adverse effect on gelling properties since finely-ground clays tend to show less gelling than coarsely-ground clays. Various other physical and chemical addition processes also have an effect on final product properties. Extrusion improves the rate-of-yield, absorptive and adsorptive properties of the clay. MgO or other alkaline additives vastly improve viscosity building properties of the gelling clays when post-added or pugged into the clay prior to extrusion. Two stage thermal processing during the drying process results in different product properties than one stage drying -- two stage processed products are less sorptive, less dusty, harder and more resistant to attrition than one pass products.

The aim of processing variations practiced is to produce three general grades of clay products, HVM, RVM and LVM, in several particle sizes as a result of heat treatments and crushing/grinding.

1) HVM (High Volatile Material) or Colloidal Gelling Grades are used as gel-producing agents in water or organic liquids. They are generally powders.

2) RVM (Regular Volatile Matter) Grades are absorbent/adsorbent grades for organic liquids. They are dried at lower temperatures and slake (disintegrate) in water or water solutions. They are produced as powders or granular materials.

3) LVM (Low Volatile Matter) Grades are absorbent/adsorbent grades for absorption of aqueous or organic liquids and adsorption of polar contaminants from nonpolar organic liquids. They can be powders or granules. They are dried at higher temperatures and do not slake in water.

Thermal processing ranges from low to high temperatures where HVM<RVM<LVM grades. Crushing gives different sizes. Coarse products are termed granulars and range from 6 mesh (3.36mm) to 100 mesh (0.149mm). Powders are finer than 100 mesh (0.149mm). Often the granular grades are closely sized and range from 6/30 (3.36/0.149mm) mesh to 50/100 (0.297/0.149mm) mesh. Powders finer than 100 mesh (0.149mm) can also be sized to 100/200 mesh (0.149/0.074mm), minus 200 mesh (-0.074mm) and minus 325 mesh (-44um). Finer powders can be purified to some extent during grinding by grinder desanders or by post air classification.

Wet Processing: Has been utilized to degrit (remove sand, calcite, dolomite, etc. particles) the clay. This involves dispersing the crude at 25% to 35% solids in water with a condensed phosphate chemical dispersant; removing undispersed particles by sedimentation and mechanical wet classifiers; adjusting the clay solids content to approximately 25% and shipping as a predispersed clay slurry. Other dispersible clay-type contaminants such as montmorillonites are not removed in this process and remain in the final slurry product.

More processing details for each type and grade are given below.

Processing Details of Various Grades of Attapulgite

HVM (Colloidal or Gelling) Grades: These grades are selectively mined (based on lab testing) to yield products with good viscosity building properties. Processing comprises the following techniques:

1) Primary Crushing and assignment to low, high and medium viscosity stockpiles.

2) Crude Blending to produce a desired viscosity range.

3) Secondary Crushing (optional) to reduce rock (calcite or dolomite) size.

4) Pugging (optional) for mixing water and chemical additives in to the crude.

5) Extrusion (used after pugging) to complete the blending of additives and/or to form a uniform shape/size for drying and to improve gelling properties of the final product.

6) Drying in a rotary drier or in a heated mill.

7) Grinding with a roller or hammer mill which may be heated for simultaneous drying. Removal of a part of the difficult-to-grind particles may be accomplished in the grinding process.

8) Regrinding -- For finer HVM gelling grades, Step #7 "grinder discharge" may be subjected to a finer hammer mill grind in a second mill. For gelling grades this may also be accomplished in other equipment such as an air fluid energy mill (jet mill) using cold air. RVM and LVM grades may be fluid energy milled with hot air or steam.

9) Classification -- The product from #8 may be subjected to a further clean-up by separation in an air classifier. The coarse rejects may be discarded or reground in Step #8. If #8 and #9 are carried out in closed circuit the grit is reground to a fine particle size (generally <44um).

The viscosity building properties of the colloidal grades are enhanced by the addition of alkaline additives (such as MgO, Na_2CO_3, etc.) to the clay during the pugging step or as a post additive after grinding and classifying. Predispersed slurries (about 25% clay in water) which can be prepared in the clay supplier's plant, as previously described, also can easily be prepared in the field by colloidal grade clay purchasers (Floridin, 1981). Predispersed gelling grade attapulgite products exhibit excellent viscosifying and gel building properties when flocculated by salts or polyvalent cations. This phenomenon is believed to be due to the fact that the prior use of chemical dispersants decreases the amount of mechanical work input required in the dispersion-flocculation process normally prescribed for such applications.

RVM (Absorbent-Adsorbent) Grades: After selective mining the products are processed using the following techniques:

1) Primary Crushing and an assignment to various stockpiles (low, medium and high absorptivity).

2) Crude Blending to produce the required sorptive capacity.

3) Secondary Crushing (optional) to adjust drier feed size.

4) Drying -- This step can be carried out in a rotary drier or a fluid bed drier. Heat input is adjusted to yield drier discharge with a free moisture (FM) of 3% to 9%.

5) Crushing and Sizing -- Crushing is carried out with roll crushers and the discharge is sized to various required meshings with a series of screens. Oversize is recycled; undersize can be reconstituted or further ground to sizes <100 mesh (<0.149mm) which are powdered grades.

Notes

1) Reconstitution -- RVM fines can be reconstituted to generate a lump drier feed by pugging water into the fines and extruding. The extrudate is then fed to the dryer as a blend with crushed crude. Products made from reconstituted attapulgite are slightly softer, more absorbent and more adsorbent than products made directly from the crude. This capability is unique to attapulgite since the reconstitution of many other absorbent grade minerals result in an unacceptable loss in hardness and sorptivity.

2) Sorptivity -- Sorptivity of clay absorbents appears to be an inverse function of the apparent density of the clay. This relationship is shown in Figure 1. Thus, if during the crude testing core samples are lab processed into granular absorbent grades and the free fall densities of the products are obtained along with sorptive capacities of the products a correlation can be established which enables the plant to use apparent densities to predict and sort the clays out into low, medium and high sorptivity types and to dictate desired blending ratios. This correlation exists because densities are higher and sorptivities are lower as the nonabsorbent mineral content of the clay increases.

3) Water Disintegration Properties of RVM Granulars -- RVM granular grades slake or disintegrate when contacted with water. This is the result of the relatively mild drying conditions used in processing -- enough water is driven off to result in a material with a respectable sorptive capacity but the degree of heating involved does little to fuse the structure together. Slakability is desirable in many granular agricultural applications (pond treatments or where rain water disintegration is desired in agricultural uses) but limits uses as will be described later.

LVM (Absorbent-Adsorbent) Grades: As described in the RVM section, these grades are selectively mined based on lab apparent density testing. They differ from the RVM grades in the higher degree of heat treatment employed in their processing which results in a granular product that does not slake in water. Thus LVM and RVM grades involve similar processing steps although variations are practiced. LVM grades are plant processed with two different techniques:

1) One Step, High Temperature Drying -- When this technique is employed crushed crude is fed to a high temperature dryer (900°F; 482°C). The discharge is cooled, crushed to a desired top sized and screened into desired granular distribution ranges. Fines are ground to <100 mesh (0.149mm). Fines cannot be reconstituted.

2) Second Step, High Temperature Drying -- RVM presized granular products (see under RVM) are the feed for a second high temperature drier (900°F; 482°C). The high temperature drier discharge is cooled and, if necessary, rescreened through sifters to remove small amounts of oversize and undersize materials.

LVM granular grades are harder (more resistant to attrition and breakdown) than comparable RVM grades. They have a lower surface area than HVM or RVM grades and, on a dry clay basis, are slightly less sorptivity than RVM grades. Because they do not slake, LVM granular grades can be used as absorbent carriers for water solutions of pesticides and to absorb aqueous spills.

Notes

1) Sorptivity or liquid holding capacity (Sawyer, 1985) -- Sorptive capacity for liquids (water and organics) is a vague term that means different things to different absorbent users. For example, granular pesticide processors require a final product that is dry and flowable when they use granular clay as an absorbent carrier for pesticide liquids. They cannot tolerate a wet granule that would prevent flowability or seep through the bags used as containers during storage and shipping Users of granular clay as pet litters and industrial floor absorbents, on the other hand are not as worried about how wet the product gets since generally the wetted absorbent is stored in a trash can and often a second clean-up application follows the initial absorption. This being the case, different sorptivity evaluations are performed for agricultural (ag) carriers and pet litter/ industrial absorbents. Ag carriers are evaluated to a dry sorptivity test endpoint as described in ASTM STP875 (1985). Pet litters and industrial absorbents are evaluated with a wet endpoint test such as the Westinghouse or Van Trump tests (ASTM STP875-1985). With 6/30 mesh (3.36/0.59mm) granular LVM attapulgite th following sorptivity ranges are encountered.

Dry Endpoint Test -- 30 to 36% liquid
Wet Endpoint Test -- 46 to 52% liquid

One type of test cannot be used to predict results with the other type of test since different phenomena are involved. Dry endpoin abortion is strictly absorption that occurs i the granule; wet endpoint absorption is a measure of liquid held within the granule, on the surface and within voids between particles Surface available and void volume depend on such factors as particle size distribution and angularity which have minor effects on granula liquid holding capacity to a dry endpoint.

2) Hardness -- Defined as resistance to breakdown (resistance to attrition) during

handling. Handling includes mechanical action during: (a) plant processing and movement, (b) shipping, (c) impregnation, (d) subsequent shipment to the field, and (e) field application for ag grades. Industrial absorbents may also be challenged by people walking on them in the wet or dry condition. Hardness is measured by such tests as ASTM E728-80. Hardness of attapulgite granular grades ranges from high (good) to low (poor) in the series LVM (two drying steps) >LVM (one drying step) > LVM (reconstituted) >RVM.

3) Screen Distribution (Particle Size Distribution) -- An important aspect of and a purchasing specification for absorbent grade attapulgite products is screen distribution. Various screen distributions result from the crushing and sizing operations on heat treated products. Granular distributions are determined by ASTM E726-80. Some rules of thumb for the absorbent-grade granular fuller's earth absorbents are:

a. Granular sizes range from 4 to 100 mesh.
b. Narrower size ranges are generally supplied. These are designated by screen ranges such as 8/16, 16/30, 20/40, 25/50, 30/60, 60/100, etc. (U.S. Standard Sieve Series). Such designations indicate that 90% by weight of the product lies between the stated screen values (such as 30/60) and that no more than 5% of the product is finer than the second mesh size.
c. Item b is often superseded by values given on customer specifications. Since customers are particularly interested in fines in the product, they may include maximum values on a 30/60 granular grade for -100 mesh, -200 mesh, etc.

4) Apparent Density -- Apparent densities as both free-fall bulk density and packed density are of importance in such matters as storage bin sizes for bulk materials and bag sizes and show relationships to sorptivity and particle counts. Free-fall bulk density can be determined by ASTM E727-80 or similar methods. Packed or tamped densities are very close in value to free-fall densities for granular carriers. For finer products packet density values assume more importance. One suitable test is described in Whittaker, Clark and Daniels, WC&D Test Method #112, "Apparent Density - Tapped Bulk - Fine Powder".

Current Commercial Applications of Attapulgite Products

The two major tonnage uses of attapulgite products in commercial applications are for absorption and gelling. Absorptive and gelling uses are followed in importance by a variety of smaller applications such as adsorption, binding, filling, etc.

Absorptive Uses (see Table 2): This is the largest use of attapulgite. Absorptive uses can be further broken down into pet litters, industrial absorbents and agricultural carriers.

1) Pet Litters are RVM and LVM granular grades. Both grades will adsorb small amounts of odors emitted by animal waste products. The RVM products absorb larger amounts of liquid waste than the LVM products but in the process tend to slake and mud.

2) Industrial Absorbents are generally RVM and LVM granular grades. They are used to clean up spills of organic liquids and water solutions as well as to immobilize both types of liquids that contain toxic contaminants during containerized shipments. The so-called floor absorbents are generally restricted to granular LVM grades because they are harder than RVM grades and nonslaking when absorbing water. These properties are important because often the user will spread the absorbent on nontoxic spills and workers will walk on the absorbent and expect nonslip footing. The nonslip feature is not recommended since the supplier recommends the products only for spill clean-ups but it is the way many users employ the floor absorbents in practice.

For liquid toxic waste immobilization the less expensive RVM granular grades are used in a container, such as a steel drum, to soak up and immobilize liquids. During handling or during truck or rail car transportation this combination package will not allow liquid to leak out even if an accident occurs and the container is ruptured. In this use the supplier of the absorbent only guarantees the physical soaking up of the liquid waste and does not guarantee that the absorbent will: (a) cause the offending liquid to lose its toxic or corrosive nature due to absorption or (b) prevent subsequent leaching or displacement by other liquids when the container integrity is disrupted during handling, shipping or burial in landfill. Often the shipping container is lined with a plastic inner liner. Typical liquids shipped using this technique have been spent battery acid (sulfuric acid), spent cyanide and phosphate metal processing water solution compounds, used lubricant oils and many others.

3) Agricultural Pesticide Carriers (Van Valkenburg, 1978; Sawyer, 1983) -- Because of favorable economics, good sorptivity, availability and good product uniformity RVM and LVM granular attapulgite products and powders enjoy wide usage as carriers for agricultural pesticides such as herbicides and insecticides. RVM granular grades are less expensive than LVM grades because less energy (lower temperature heat treatments) is employed in their preparation. RVM granulars are used when:

a. the free moisture on the granule does not adversely affect the impregnated compound.
b. the impregnating compound does not slake the granule (water solutions cannot be used).
c. the user desires disintegration of impregnated granules after application to hasten release and to allow better distribution. This is the case when the product will be used in pond treatments, forest floor treatments and treatments of many crops.

LVM sorptive grades are used when:

a. Water solutions of pesticidal compounds will be impregnated.

b. The pesticidal compound is sensitive to water (free moisture) on the carrier.

c. Higher sorptivity, harder granules are required to minimize mechanical breakdown and maximize sorptivity.

d. Less rapid release and no slaking after application are specified.

Granular grades (RVM and LVM) furnished to agricultural formulators and others range through 8/16 (2.38/1.19mm), 16/30 (1.19/0.59mm), 20/40 (0.84/0.42mm), 25/50 (0.71/0.297mm), and 50/100 (0.297/0.149mm) sizes. These grades are supplied in bulk and bags. The customer processes them by removing fines in a prescreening operation, impregnating and rescreening fines from the final product. Powdered grades of RVM and LVM attapulgite are supplied in bulk and bags. Processing can consist of an impregnation blending of liquids on to the powdered clay or the co-grinding of solid pesticide compounds plus the clay to produce dusts and wettable powders. Often other components besides pesticides are absorbed on both granular and powdered attapulgite products in such products. These can include deactivators for the clay, surfactant blends (wettable powders), solvents for pesticidal compounds (water or organic liquids), higher sorptivity carriers and less sorptive diluents. Many times impregnations are carried out at elevated temperatures in heated equipment in order to increase solubilities of the pesticidal compound in a solvent and/or to liquify a low melting point compound.

4) Anticaking -- Powdered LVM grades of attapulgite are used as conditioning agents for ammonium nitrate (explosive and fertilizer grades), urea, resins, fertilizers, etc. They function by coating the solids (granule, prill or flake) and absorbing solvents that are present or water condensed from the air. This retards the growth of bridging crystals.

5) Soil Adjuvants -- LVM granular and powdered grades are added to potting soils in greenhouses and seedling soils when setting out trees (Koo, 1967). As a component in soil blends they can be saturated with water and/or liquid fertilizers to serve as a reservoir for these ingredients that are essential to growth. Attapulgite is particularly effective in retaining water in rapidly leached, rapid-draining, sandy soils and has been widely used for the planting of citrus tree seedlings. LVM granular attapulgite products (6/30) are incorporated into poor-permeability clayey soils and shales to improve drainage in golf courses and athletic fields. LVM granular attapulgite is used on baseball fields to dry up rain puddles in base paths.

Adsorbent Applications (see Table 3): At one time the use of RVM and LVM attapulgite powders and granules as adsorbents consumed the major share of attapulgite mined in the U.S. Primarily the attapulgite was involved in cleaning up and decolorizing petroleum products with smaller amounts being used for animal fats and vegetable oils. Competing technologies, in part, have replaced these applications but many uses still remain and new ones have been developed. Generally attapulgite products function in purification/decolorizing by selectively adsorbing or reacting with impurities in liquids. Certain more polar contaminants preferentially interact with the clay surface and are removed from liquids where the molecules in the bulk of the liquid show less affinity for the clay surface. Often differences in polarity are reflected in this adsorption with more polar molecules being absorbed; often certain chemical characteristics such as ionic character and conjugate double bonds in cyclic and aliphatic organic compounds (many times these are color bodies) show preferential adsorption. Adsorption phenomena range from physical adsorption through chemi-sorption to chemical reactions. In all instances adsorption is a solid surface interaction with a contaminated liquid adsorbate to remove some of the undesirable molecules. It is not a bulk phenomenon as is absorption although some purification operations involve both adsorption and absorption. The clay also has the ability to interact with certain colloids and colloid size particles such as viruses (Morton, 1976) and remove them from liquids. Usually the rate and efficiency of such uses are related to available clay surface and thus to particle size.

Two techniques are used in adsorptive processes. They are percolation and contacting.

Percolation is the passing of a liquid through a granular bed of clay in a column where the bed might be static, fluid or moving and where the passage might be co-current or countercurrent. Granular clays used in percolation are often thermally treated prior to use and are regenerated for reuse by using solvent washing, steaming and thermal processing.

Contacting is the treating of a liquid with fine granular grades and powdered adsorbent clays while stirring, followed by clay removal by settling and filtration. In both processes the adsorbent is thermally processed to remove volatiles and maximize adsorptive processes (activation) prior to use and the process is performed at varied temperatures to optimize surface-contaminant interaction. Contacting process filtration rates and retentions may be improved by the use of filter aids by precoating and/or body feeding. Clays used in contacting may be steamed or solvent washed to recover more product but never are regenerated for reuse.

Some examples of the commercial use of adsorbent grades are listed below:

1) Petroleum Refining -- A tower or column is packed with a bed of 4 mesh at the bottom, 8/16 as the next layer and 6/30 LVM attapulgite at the top. This is used to remove $AlCl_3$ catalyst from a liquid isomerized stock stream. The adsorbent is not regenerated.

2) Kerosene Decolorization -- 25/50 LVM clay is used in a column to improve the color of a kerosene distillate fraction. This column can be regenerated.

3) Re-refining -- 200/up RVM clay is used to decolorize and neutralize acidity in an oleum-treated and desludged used engine oil in a contacting operation.

4) Transformer Oil Regeneration -- Used transformer oil is contacted with 50/100 LVM clay or percolated through 30/60 LVM granular clay to improve the color and dielectric constant. Normally the clay is not regenerated.

5) Jet Fuel Treatment -- Stored jet fuel is percolated through a bed of 30/60 LVM granular clay to remove water, surface active materials and bacteria prior to placing it in a tank truck or ready tank at the airport. This clay is not regenerated.

6) Vegetable Oil -- Powdered RVM clay is contacted with vegetable oil to improve acid numbers and color. The clay is filtered out. No generation is practiced.

7) Antidiarrheals -- Powdered clay is used in veterinary and human pharmaceutical preparations to control diarrheal by adsorbing viruses and toxins (Barr, 1957).

8) Cartridge Component -- LVM granular grades are used as components in preformed filter cartridges for the cleaning of oils, mineral spirits and perchlorethylene dry cleaning fluids, and other organic liquids.

9) Water Purification -- Powdered clay is used in commercial and potable river water treatments in conjunction with alum-lime treatments. The clay adsorbs viruses, reduces acidity and functions as a floc weighting agent. It also flocs soil colloids.

Commercial Uses of Coarse-Ground Gelling Grades (see Table 4): The coarse-ground gelling grades are used in large volumes for such commercial applications as agricultural suspensions, drilling mud gelling agents, liquid animal feed supplement stabilizers, etc. These uses result from the nontoxicity of the attapulgite, the ability of attapulgite to be gelled in ionically contaminated solutions and, finally, its ability to provide viscosity-stable gelled solutions of salts. Because of these unique properties and its ready availability, attapulgite is considered to be one of the most important gelling clays. It is not a swelling clay like Wyoming bentonite and thus is not subjected to the interferences of ionic contaminants and the flocculating effects of polyvalent cations that W. bentonite exhibits. Attapulgite HVM (colloidal) grades will gel in saturated solutions of $NaCl$, $CaCl_2$, $MgSO_4$, $CaSO_4$, NH_4NO_3, ammonium phosphates, KCl and many other salts. This unique property plus the excellent stability of the resultant gels differentiates the colloidal attapulgite clay products from many other gelling/viscosity producing agents such as the natural and synthetic polymeric organic hydrocolloid gums, Wyoming bentonite, hectorite and others since they will not gel in ionically contaminated water solutions. Furthermore, if the other gelling agents are previously gelled in uncontaminated water, their gels and viscosifying effects are not stable when ionic material is introduced, particularly solutions containing polyvalent cations. As one would anticipate, these unique characteristics of the HVM attapulgite products result in many industrial uses where other gelling agents will not perform satisfactorily or only with great expense and difficulty. Some of these attapulgite applications are listed in Table 4 and described below.

1) Agricultural Suspensions and Emulsions NFSA, 1978; Wolford, 1983) --

a. Liquid suspension fertilizers are water solutions of plant nutrients plus nutrient ingredients in excess of their solubility. Colloidal gelling clay is added to stabilize this mixture by suspending the undissolved nutrient particles. Suspension fertilizers contain nonionic material (urea) and many types of ions (K, Cl, NH_4, NO_3, SO_4, PO_4, Mg, Ca, etc.). The ability of formulators to produce these stable suspensions has enabled them to economically compete with the high analysis mixes of dry fertilizer manufacturers while still keeping the advantages of liquid fertilizers -- easier, more uniform application, the co-application of solid and liquid pesticides, co-application of soil neutralizing agents, drift control, and others.

b. Tank mixes are mixes of immiscible liquid and/or insoluble powdered solid pesticides in water or liquid fertilizers as carriers (Wolford, 1983). They are stabilized in either type of carrier liquid by the incorporation of gelling grade attapulgite. The attapulgite gels the continuous aqueous phase and thus prevents creaming and floating of an immiscible liquid phase and agglomeration and settling of a solid insoluble phase. Often one pass over a field can be used to apply a stabilized suspension fertilizer containing one or more liquid and solid pesticides. In a similar manner solid neutralizers such as finely ground calcitic lime or dolomitic lime can be used as the insoluble solid in attapulgite-stabilized water or liquid fertilizer suspensions (Wolford, 1977). A successful extension of this technique involves hydroseeding of such small seeds as grasses, clover, alfalfa, wheat and others as a clay-stabilized suspension in water and liquid suspension fertilizer tank mixes (Wolford, 1984).

c. Liquid Animal Feed Supplements contain ionic materials (NH_4, K, Cl, Na, trace nutrients) plus non-ionic materials (urea, molasses, vitamins) plus insolubles such as calcitic lime, animal fat emulsions and vegetable oil emulsions. A very efficient way to produce a stable uniform mixture of these components is to gel them with colloidal (HVM) attapulgite and thus prevent settling of the solids and floating of the fats and oils. When such a mixture is solidified into a solid range block, clay is employed to stabilize the liquid suspension-emulsion until it reacts and solidifies (Wolford, 1984).

Notes

1) Clay Addition Techniques -- In the clay-stabilized agricultural suspensions

and emulsions the gelling of the clay is accomplished using three techniques:

- a. Addition of the dry powdered clay as a final ingredient while mixing.
- b. Pregelling the clay at the 10% clay level, while agitating, in a liquid component of the mix. This is followed by adding other ingredients to arrive at the desired final clay concentration (2% to 5%).
- c. Predispersion with a chemical dispersant in water (and agitating) using the formula:

	%
Water	74.25
Tetrasodium pyrophosphate	0.75
Gelling grade attapulgite	25.00
	100.00

The predispersion is then mixed in during processing at a point where the clay is about 5% to 7% of the total mix and then other ingredients are added to finish the batch (Floridin, 1981) and arrive at the desired analysis.

Efficiency of clay usage of these incorporation techniques as measured by gel strength and viscosity development is c>b>>a.

2) Rheological Characteristics -- Rheological characteristics of clay stabilized mixtures are yield-pseudoplastic with a measurable gel strength and thixotropy. Gel characteristics contribute to suspension and emulsion stabilization when the mix is at rest. High low-shear viscosities result in a stabilizing effect when the mix is subjected to low shear during transfer pumping and shipment. Furthermore, low high-shear viscosities are a plus factor during spray application. An important characteristic of the clay-thickened liquids is recoverability -- when mixes are shear-thinned at high shear rates, gel strengths and high low-shear viscosities are rapidly recovered after high-shear is discontinued. Other important points related to the successful industrial use of gelling grade attapulgite products are uniformity from lot-to-lot and availability in large quantities.

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2) Oil Well Drilling Fluids (Sawyer, 1983 and 1986) -- Colloidal attapulgite gelling clays are used in water-based oil well drilling muds when:

- a. The water to be used is contaminated with ionic materials (Na, Cl, Mg, Ca, SO_4), as with sea water, brines, etc.
- b. When fresh water is available but accidental or deliberate contamination during drilling from brines or salt, gypsum, anhydrite, etc., deposits is anticipated.

The fluid when circulated serves to remove cuttings from the well, to cool and lubricate the bit, to seal liquids out of formulations, to balance ground hydrostatic pressures, and to prevent gas intrusion when the mud is treated with appropriate additives such as thinners, weighting agents, shale hydration inhibitors, starch, etc. Attapulgite is used also to stabilize cement slurries for insertion as lightweight plugs into the well.

3. Caisson and Foundation Drilling (Sawyer, 1986; Williams, 1985) -- Gelling grade attapulgite is used for two types of caisson drilling where ionic contamination will be encountered in the water-based drilling fluid employed. The first involves deep cavities where the fluid is recirculated to remove cuttings from a rotary drill. After the hole has been established, reinforcing rods are inserted and concrete is poured in to replace the mud. The composition used in this application and its functions are very similar to those described in oil well drilling.

The second type are shallower excavations where a brackish high water table is encountered and an auger is used. No recirculation is involved and the auger is lifted to remove spoil. The attapulgite mud is pumped in to prevent hole collapse and sloughing from the high water table during auger drilling and drill removal. After the caisson has been bored the auger is removed, the bottom is cleaned out, reinforcing rod is inserted and concrete is poured in to displace the mud.

4. Forest Fire Fighting Liquids -- These water-based solution fluids contain dissolved ammonium sulfate or ammonium phosphates. They are applied by aerial drops from tanker planes or by ground spraying. It is desirable that the fluids wet and cling to foliage and twigs to retard ignition in the path of fires. Adding gelling grade attapulgite thickens these ionic solutions and increases the amount that adheres to combustibles. Furthermore, when dropped from planes the gelled fluid forms larger droplets than ungelled solutions and show less drift, lower evaporation rates and good adhesion.

5. Impermeable Soil Barriers (Tobin, 1986) -- Gelling grade attapulgite is used as a component of nonstructural cut-off walls to adjust soil permeability and thus control seepage from scenic ponds, waste ponds that are plastic lined, sanitary landfills, etc. Attapulgite with its ability to disperse in and gel ionically contaminated fluids works particularly well where intruding and leachate water contains dissolved salts -- sea water intrusion, waste chemical ponds, industrial landfills, retention walls around tanks that contain ionic solutions -- and is currently used for these applications.

6. Asphalt Emulsions -- Attapulgite stabilizes asphalt emulsions in water by thickening the continuous water phase to prevent agglomeration and creaming. The emulsions are used in driveway and foundation sealing.

7. Cement Grouts -- Cement slurries can be kept uniform by the incorporation of small amounts of gelling grade attapulgite. This allows them to be pumped through pipe lines and delivered to specific sites without segregation.

Commercial Uses of Fine Ground Gelling Grades in Water-Based Compositions (see Table 5): The coarse ground gelling grade attapulgite clays, mentioned in the previous section, are excellent additives for producing gel and viscosity properties in water systems, however, because of their coarse grit content they are not usable in some applications and finer ground grades (where the grit is reduced in particle size and/or removed) are required. Some of these applications are listed in Table 5. It should be noted that all of the attapulgite characteristics and make-down techniques previously described are true for the fine ground clays. The following examples give a good background for such uses:

1) Tape and Joint Compounds -- Gelling grade attapulgites have been used successfully in these compounds to replace asbestos. The compound consists of a water system containing fillers, adhesives and stabilizing agents that control gel and viscosity. The gel-viscosity control agents used are attapulgite and a variety of organic-polymeric thickeners that function as stabilizers until the mix is applied. They also contribute to application characteristics. After application the mix dries and must not exhibit much shrinkage or develop sag, bubbles or cracks. If necessary, the dried compound should sand easily. Fine ground attapulgites are used because of their rheological characteristics, availability and economics. This is a medium tonnage use.

2) Latex Paints -- Fine grind grades are added to latex paints in small amounts to stabilize suspensions of the pigments and extender fillers and to contribute to gel and viscosity properties to obtain the desired sag, flowability and application features characteristic of modern latex paints. Attapulgite products are used in conjunction with cellulosic thickeners to achieve these properties.

3) Molecular Sieve Binders -- Molecular sieves used as adsorbents are consolidated into larger particles using colloidal grades of attapulgite as binders. Attapulgite gelling grades are used because they bind adequately with minimal interference with the sorptivity characteristics of the sieves.

4) Suspension-Emulsion Stabilization -- This use has been described under the coarse-ground grades. Fine ground gelling grades are employed as stabilizers in situations where erosion and grittiness must be minimized. When agricultural pesticide flowable emulsions and suspensions are sprayed in small amounts per acre, nozzle erosion can drastically alter calibrations. In cosmetic and pharmaceutical preparations grittiness is considered to be undesirable. Pigment suspensions are often ground to finer than 0.5um and a gritty stabilizer cannot be tolerated.

5) Adhesives -- To keep the glue at the glue line fine colloidal attapulgite grades are incorporated in phenol-formaldehyde and resorcinol-formaldehyde wood adhesives. The attapulgite-thickened adhesive exhibits less substrate penetration and squeeze-out during prepressing. An added bonus results from the water-holding capacity of the attapulgite. Since the clay retains moisture, which is necessary in the hot press curing operation, much longer open times can be tolerated. Thus the attapulgite acts as a thickener and moisture reservoir.

6) Coal-Water Slurries (Purcell, 1984) -- As a replacement for high priced oil and gas fuels for generating heat, steam and power, dry powdered coal and slurries of 70% coal in water were evaluated as fuels in the late 70's and early 80's. The use of dry coal is quite common but coal-water slurry uses are much rarer. One of the major problems that face coal water slurry users was settling. Colloidal grade attapulgite at the level of 0.5% has been gelled in such fuels to give a stabilized, combustible mixture.

Commercial Uses of Fine Grind Gelling Grades in Gelling Organic Liquids: Some of the finer ground colloidal attapulgite gelling grade products are specially sized and processed for use in gelling organic liquids. These liquids include aromatic and aliphatic hydrocarbons, esters, higher alcohols, asphalt, asphalt cutbacks, lubricating oils, chlorinated aromatics and aliphatics, and others. To achieve this thickening effect, the attapulgite must be used in conjunction with suitable surfactants (surface active agents) which aid in clay dispersion and play a role in the gel structure formed. Cationic organic surfactants -- such as amines, amine salts, quaternary ammonium salts, imidazolines, and others -- generally appear to be suitable surfactants for most liquids. There are types of nonionic surfactants such as alkylphenol ethylene oxide condensates and amine oxides, that are suitable as well as anionic alkanol amine fatty acid salts. Many references exist on important parameters in the gelling of attapulgite clay-surfactant mixtures in organic liquids (Haden, 1967; Floridin, 1985; Engelhard, undated; Floridin, 1984). Ingredient, processing and formulation variations that are significant are clay grind (fine is desirable), clay free moisture, type of surfactant, clay to surfactant ratio, processing equipment used (high shear is best), and processing techniques used. For economic reasons a high clay to surfactant ratio is desirable -- about 7/1 to 8/1 -- since the surfactants are costly. Clay free moistures of 10% to 16% are necessary since in the dispersion step the surfactant aids in dispersing the clay through the water layer that surrounds clay crystals. To increase work input during the agitation (shearing) step, the pregelling process is advantageous. Pregelling consists of agitating the clay plus surfactant at the 15% to 20% clay level in the organic liquid until a gel is formed. Other ingredients, liquids first and then solids, are blended in until the formulation is completed and all components are present at desired levels. Viscosity or consistency of the final product is important and may be measured with a viscometer (for flowable liquids) or a penetrometer (for greases). Stability of consistency is also important and is determined by periodic testing during storage. Attaplugite clay-surfactant gels exhibit gel strengths and are thixotropic. Flow characteristics are described as yield-pseudoplastic.

Examples of products in which attapulgite clay-surfactant gels are utilized are listed in Table 6 and below:

1) Alkyd Paints -- Colloidal attapulgite and Monazoline T (Mona Industries), a tallow imidazoline, are added to alkyd paint to suspend pigments and control sag and flow. The clay-surfactant is gelled into the liquid in a roll milling step or with medium shear agitation in the alkyd.

2) Asphalt Cutback Coatings -- Colloidal attapulgite and Aquad 2C (Akzo Chemie America), a quaternary ammonium compound, is used to gel aliphatic solvent asphalt cutbacks used in roof coatings and automotive undercoating. The purpose of using the clay-surfactant mixture originally was to remove asbestos from the formulation. For a complete asbestos replacement the use of clay-surfactant must be accompanied with an addition of an innocuous fiber (such as cellulose or polyolefin fibers) since asbestos is a fibrated thickener. Nonfibrated formulations do not require any fiber addition.

3) Naphtha Core and Mold Washes -- Colloidal attapulgite-Amine O (Alrose-Geigy), an oleic acid imidazoline, is used to gel a blend of low residue naphtha and flake graphite. The clay-surfactant gel uniformly suspends the graphite to form a concentrate. This is let down, one volume of concentrate to three volumes of naphtha, and sprayed on the cavity of the foundry mold and on cores to improve casting finishes.

4) Petroleum Oil Greases -- Are gelled with colloidal clay-Arquad 2HT (Akzo Chemie America), a quaternary ammonium compound, at a 10% clay level and 6/1 clay to surfactant ratio. Processing is accomplished with a colloid mill. Such greases exhibit good mechanical stability, good lubricity, and excellent resistance to water pickup. High temperature properties are excellent since the clay is a mineral and does not dissolve in the oil. Abrasion of metal parts is as good as soap greases if the clay has been degritted.

5) Coal-Oil Slurries (Sawyer, 1978) -- Fifty-fifty blends of fuel oil and powdered coal are being burned as an alternate to fuel oil and gas. The powdered coal tends to settle and the blend can be stabilized by the addition of 1% colloidal attapulgite along with Monazoline T (Mona Industries) at a 5/1 clay to surfactant ratio. The clay-surfactant is gelled in the fuel oil.

Summation

Commercial uses are described for granular and powdered adsorbent and absorbent attapulgite grades and for coarse and fine grind colloidal (gelling) attapulgite products. Relationships between prescribed properties resulting from selective mining and processing variations are established and related to final products and their commercial fields of application. Major areas of application for attapulgite products are in gelling water and organic liquids, absorption and adsorption. Specific markets for absorbents are industrial floor absorbents, waste liquid immobilizers, pet litters and agricultural pesticide carriers. Markets for adsorbents are kerosene treatment; jet fuel treatment; re-refining of used motor oil, transformer oil and metal roll oils; and refining of vegetable oils and animal fats. Markets for the utilization of coarse ground attapulgite gelling grades are salt water drilling muds, liquid agricultural suspensions (fertilizer, lime, sulfur and pesticide tank mixes), liquid animal feed supplements and range blocks, soil permeability control and water-based stipple paints. Fine ground attapulgite gelling clays are used in both the gelling of water systems and organic liquids to impart stability and desired rheological characteristics. The fine ground gelling grade products are used in joint compounds, spackles, caulks, paints, molecular sieve binding, agricultural pesticide emulsion and suspension stabilization, asphalt cutback coating compositions, coal-oil and coal-water slurries, wood adhesives and many other applications.

As can be seen the unique clay mineral attapulgite has a wide variety of uses that are continually changing by the addition of new applications. These uses have resulted from the ready availability and favorable economics plus the large amounts of R&D that have been expended in selective mining and plant processing to ensure usability and uniformity of the attapulgite products.

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Table 1. Properties of Commercial Attapulgite Products

	Property	Type of Field Uses
1.	Gelling:	
1.1.	Water Systems --	Gels ionically contaminated solutions, gels multiphase systems (emulsions and suspensions) where the continuous phase is water or a solution, stabilizes latex products. The clay is added for stabilization, rheology control, thickening/gelling, filling with delayed gelling, penetration control, etc.
1.2.	Organic Liquids --	Can be used in conjunction with a surfactant to gel liquid hydrocarbons (aliphatic and aromatic), higher molecular weight alcohols, esters, aldehydes, ketones, asphalts, asphalt cutbacks, etc. Gels certain organics such as glycols, diisocyanates and polysulfides without the use of a surfactant. The clay is used for suspension stabilization, gelling, flow control, pseudoplasticity, control of sag, flow properties, penetration control, etc.
2.	Absorption:	For cleaning up liquid spills, as a carrier and diluent for dry-applied functional liquids, for containing liquids during transportation (immobilization).
3.	Adsorption: (and reaction)	For removing impurities from liquids; for neutralizing acidity; for catalyst removal; for adsorption of alkaloids, viruses and toxins.
4.	Miscellaneous:	Binding, penetration control, water release characteristics, soil conditioning, etc.

Table 2. Commercial Uses of Absorbent Grades

(Grades in Parentheses)

1. Pet Litters (LVM and RVM granules)
2. Industrial Absorbents
   - a. Floor Absorbents (LVM granules)
   - b. Liquid Waste Containment (LVM and RVM powders and granules)
3. Agricultural Pesticide Carriers (LVM and RVM powders and granules)
4. Conditioner Anticaking Agents (LVM and RVM powders) - ammonium nitrate, urea, finished fertilizers, fire extinguisher chemicals
5. Soil Adjuvants (LVM powders and granules)

Table 3. Commercial Uses of Adsorbent Grades

(Grades in Parentheses)

1. Petroleum Refining
   - a. Percolation (LVM granules)
   - b. Contacting (RVM and LVM powders and fine granules)
2. Petroleum Re-refining
   - a. Contacting clean-up of used engine oils (RVM powder)
   - b. Contacting of used transformer oils (LVM powders and granules)
   - c. Contacting of used metal rolling and metal working oils (LVM powders and granules)
3. ? Jet Fuel Clean-up (LVM granules)
4. Catalyst Removal (LVM granules)
5. Vegetable Oil Treatment (RVM and LVM powders and granules)
6. ? Pharmaceuticals (HVM and LVM powders)
7. Cartridges (LVM granules) as an adsorbent component for preformed filter cartridges for the clean-up of liquids

Table 4. Commercial Uses of Coarse-Ground Gelling Grades

1. Stabilization of Agricultural Suspensions and Emulsions
   - a. Suspension fertilizers
   - b. Lime, gypsum and sulfur suspensions
   - c. Fertilizer tank mixes that contain pesticide emulsions or suspensions
   - d. Seed suspensions in water or liquid fertilizers
   - e. Combinations of a, b, c and d
   - f. Liquid animal feed supplements that contain fat emulsions or particulate insolubles
   - g. Nutritional and medicated range blocks
2. Oil Well Drilling Fluids
3. Caisson and Foundation Drilling
4. Forest Fire Fighting Liquid Gellant
5. Soil Barrier Adjuvants
6. Asphalt Emulsions, Driveway Sealers
7. Foundry Sands
8. Cement Slurries (Grouts)
9. Texture Paints
10. Molecular Sieve Binder
11. Ag Granule Binder

[redacted]

Table 5. Commercial Uses of Fine Ground Gelling Grades

(Water-Based Compositions)

1. Tape and Joint Compounds
2. Spackles, Grouts and Sealants
3. Latex Paints
4. Molecular Sieve Binding
5. Suspension-Emulsion Stabilization
    a. Agricultural pesticide flowable suspensions
    b. Cosmetic and pharmaceutical suspensions and emulsions
    c. Resin suspensions
    d. Pigment suspensions
6. Emulsion Stabilization
    a. Agricultural pesticide flowable emulsions
    b. Emulsion cleaners
7. Adhesives
8. Coal-Water Slurries

Table 6. Commercial Uses of Fine Grind Gelling Grades

(Organic Liquid Gelling)

1. Alkyd Paints
2. Asphalts (Hot Melt Coatings)
3. Asphalt Cutback Coatings (Automotive Undercoating, Roofing Compositions)
4. Naphtha Core and Mold Washes
5. Caulks, Sealants, Putties and Glazing Compounds
6. Petroleum Oil and Ester-Based Greases
7. Coal Oil Slurries

[redacted]

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