[illegible]

[illegible]

1/1/235 November 1979

S.A. Department of Mines & Energy

Amdel Report

No. 1296

ABSORBENTS - PALYGORSKITE AND MONTMORILLONITE

by

Michael D. Ware

Investigated by: Materials Division

Manager, Materials Division: Dr William G. Spencer

Norton Jackson, Managing Director

THE AUSTRALIAN MINERAL DEVELOPMENT LABORATORIES
Flemington Street, Frewville, South Australia, 5063

CONTENTS

Page

SUMMARY

1. INTRODUCTION 1

2. TERMINOLOGY 3

   2.1 Bentonite 3

   2.2 Fuller's Earth and Activated Earths 3

   2.3 Palygorskite 5

3. SORBENT APPLICATIONS 6

   3.1 Absorbents 6

   3.2 Pesticide Carriers 7

   3.3 Wine Fining 8

   3.4 Refining and Bleaching Edible Fats & Oils 9

   3.5 Pharmaceutical Uses 12

   3.6 Textile Industry 13

   3.7 Other Industries Using Bleaching Earths 13

4. PRODUCTION AND IMPORT STATISTICS 14

5. SUMMARY AND CONCLUSIONS 15

6. PALYGORSKITE SAMPLES FROM THE LAKE FROME AREA 16

   6.1 Introduction 16

   6.2 Materials Examined 17

   6.3 Assessment Procedures 17

   6.4 Results and Discussion 18

   6.5 Conclusion 19

7. REFERENCES 21

TABLES 1 TO 12

APPENDIX A: Volclay A-1

APPENDIX B: Bleaching Test for Soybean Oil B-1

APPENDIX C: Modified Bleach Test for Soybean Oil C-1

APPENDIX D: Bleaching Test for Cottonseed Oil D-1

APPENDIX E: Refined and Bleached Color for Soap Tallows and Greases E-1

SUMMARY

Background

Samples of clay from the Lake Frome area had indicated potentially large deposits of palygorskite-rich clay of possible economic value. An investigation of absorbent clays in general was requested by the South Australian Department of Mines and Energy in order to determine the potential use of the Lake Frome materials.

Objectives

The primary objective of the investigation was to determine the markets, sources and specifications for absorbent clays in Australia. A comparison of the Lake Frome materials with specifications and commercial clays formed the secondary objective.

Summary of Work Done

A review of the market for bentonites, palygorskites and absorbents generally was carried out. Experimental work was performed on six samples from Lake Millyera, Jadliaura Creek and Lake Tarkarooloo in comparison with specifications and commercial clay products. The results showed potential markets as a low grade absorbent suitable for pet litters and industrial spillages.

Conclusions

Absorbent clays are not used extensively in Australia. Total market for bleaching earths is about 4000 tonnes per annum. Absorbent uses for oil spills, pet litter and general low grade absorption probably total some five to seven thousand tonnes per annum. Uses other than bleaching and absorbents are small and were estimated at less than 3000 tonnes since substitution by non-clay products is common but not quantifiable.

A wide variety of minerals are processed into granular and powdered forms as absorbents. Competing minerals are palygorskite, bentonite, diatomite, illite, bauxite and magnesite.

Lake Frome materials appear to be competitive with performance of these commercial products but necessitate heating to 650°C which changes their colour to red-brown. The competing materials are generally pastel buff/green colours and this may cause market resistance to Lake Frome products.

1. INTRODUCTION

Following the discovery of large deposits of palygorskite-rich clays in the Lake Frome area, the South Australian Department of Mines and Energy requested AMDEL to carry out an investigation of absorbents with the following aims.

1. Absorbent market review, including details of market, sources and specifications.
2. Comparison of Lake Frome material with specifications and with commercial absorbent clays.

A progress report comprising the bulk of the data and conclusions was issued in June 1979.

A sorbent mineral is one which, arising from its physico-chemical properties, has the tendency to either decrease its free surface energy, resulting in the phenomenon of adsorption, and/or imbibe liquids, resulting in a more or less uniform penetration of a liquid throughout its porous mineral structure. Absorption also describes the phenomenon which occurs when a gas or vapour penetrates a solid or liquid structure, often with resulting chemical reaction as in the use of quicklime for gas drying when a new compound-calcium hydroxide is formed.

Adsorption is a specific term which refers to the existance of a higher concentration of any particular component at the surface of a solid (or liquid) phase than is present in the bulk. Generally adsorption is concerned with surface layers only a few molecules thick and therefore a very large specific surface must be presented by the adsorbent if it is to be capable of carrying an appreciable quantity of sorbate and thus be of commercial interest.

Since it is generally difficult to distinguish between the effects of absorption and adsorption the general term sorption is commonly employed to include both phenomena.

A close connection exists between adsorption and catalysis, since chemical reactions based on solid catalysts involve adsorption as a fundamental part of their mechanism. Thus many of the sorbent minerals are also useful catalysts in industry.

A wide variety of industrial minerals, both oxides and silicates, figure prominently in the field of adsorption, absorption and catalysis. In particular are the clay minerals, zeolites, diatomite, bauxite and alumina chemically derived from bauxite. Table 1 (after Jones 1974) presents some general properties of adsorbents derived from industrial minerals. Of the clay minerals two types most commonly used are the bentonitic clays, or clays containing smectite minerals (predominantly montmorillonite) and the hormites (palygorskite and sepiolite).

Reference may be made to two Amdel reports, MD 1/1/210 Progress Reports 1 and 2 for a review of the structure and general properties of both palygorskite and bentonite (Bottrill & Spencer 1978, Day 1978).

This report is concerned specifically with the sorption properties and commercial applications arising therefrom of palygorskites and bentonitic clays. Since there is a confusion of terminology used in the industry it is necessary to review the various specific and common names used to describe sorbent clays prior to discussing the various applications in detail.

The number of proprietary products available in Australia is wide for sorbent applications (and many of these consist of material other than bentonite or palygorskite). Due to strong competitiveness between both suppliers and users there is understandably some reluctance to divulge specific details of products and hence detailed information is difficult to obtain. However, where possible specifications and consumed tonnages of both producer and user industries are included.

2. TERMINOLOGY

2.1 Bentonite

The term bentonite is well established for "any clay which is composed dominantly of a smectite clay mineral and whose physical properties are dictated by this clay mineral" (Wright 1968). Earlier definitions of bentonite however implied a mode of origin such as the description of Ross & Shannon (1926) "Bentonite is a rock composed essentially of a crystalline clay-like mineral formed by the devitrification and the accompanying chemical alteration of a glassy igneous material, usually a tuff or volcanic ash". This definition in part arose from the observation by geologists that the clay originally termed "bentonite" by Knight (1898) in 1898, to describe a clay, thought to occur in the Benton Shales, at the site of the first mine near Rock River Wyoming originated from transported volcanic material. Since the definition applied to a bentonite by Ross & Shannon (1926) and other workers it has been recognized that many bentonite deposits have formed from rocks other than the types required by this definition. Thus, for the term bentonite to be valid the connotation of mode of origin must be deleted and the redefinition by Grim (1972) is appropriate. "Bentonite is a clay consisting essentially of smectite minerals, regardless of origin or occurrence."

2.2 Fuller's Earth and Activated Earths

The term was derived from its early use in "fulling", or removing grease and dirt from wool (from the Latin "fullo" - I launder). The use of the term therefore originally implied a specific end use but as additional uses for the material became known the term became generally accepted.

From a mineralogical viewpoint the term "fuller's earth" has no value since it is used to describe a wide variety of materials with markedly different mineral components and crystal structures which are suitable for bleaching, absorbing and other specific uses.

In general fuller's earths consist of clays of the smectite group, notably calcium montmorillonite or hormite (palygorskite and sepiolite) clay minerals. Not all clays, however, composed of these minerals have bleaching or decolorizing capacity necessary for their classification as fuller's earths.

Fuller's earths may be natural or treated to improve their adsorbing properties. The most general form of treatment involves the use of acids, hydrochloric or sulphuric and they are then commonly referred to as activated earth, activated fuller's earth, activated bleaching clay or contact clay depending on the terminology of the user industry. Calcium montmorillonites are generally activated and although the reaction is complex Jones (1972) describes the process as one which extracts ions of aluminium, magnesium and iron (if present) from the octahedral layer and replaces the exchangeable calcium ions by cations present in the activating solution that is, predominantly by aluminium and hydrogen. Cations extracted from the octahedral layer are also replaced by hydrogen ions, while adventitious minerals such as calcite and iron pyrite admixed with the fuller's earth are decomposed and pass into solution, or, if H_2SO_4 has been used, calcite reacts to form insoluble calcium sulphate. After activation the clay is washed and dried resulting in production of a fluffy powder. Activated carbon may be added to the earth during production of special grades.

The activation process greatly increases the surface area of the clays available for adsorption (possibly from about 80 to 200 sq metres/gm or higher for calcium montmorillonite, in the case of nitrogen gas) and causes the exposed area of the clay to behave as a solid acid which is capable of preferentially attracting, or specifically adsorbing certain kinds of molecules present in crude oil and other liquids. Alternatively the same acid sites may act as catalytic centres, increasing the speed of chemical reactions such as those of cracking and alkylation. Obviously there is an optimum degree of activation depending upon the proposed application for the activated earth.

Although the principal fuller's earth deposits other than the bentonite type consist of palygorskite or sepiolite, a rock called opal clay stone consisting dominantly of poorly ordered silica and some montmorillonite, some kaolins, halloysites and glacial clays may also be termed fuller's earth due to their similarity in use to the more general fuller's earth.

2.3 Palygorskite

In 1935 J. deLapparent suggested the name attapulgite for a clay mineral occurring in certain fuller's earths of Georgia and Florida U.S.A. and in clays at Montmorillon, France.The name was coined from the area, Attapulgus, Georgia, in which it was first recognised by de Lapparent.

In 1862 Savchenkov gave the name "palygorskite", after the mineral district in the Urals, to a mineral which is now recognised as being structurally the same as attapulgite. Thus the terms may be synonomous and although both appear in the literature the name palygorskite would appear to have a better pedigree. According to de Lapparent however the term palygorskites (the fibrous clay group) should apply to the isomorphous sepiolite-attapulgite series which includes a hydrous magnesium silicate end-member, sepiolite and an assumed hydrous aluminium silicate end member, paramontmorillonite. Other common names for palygorskite (attapulgite) which appear in the literature are 'mountain cork' or 'mountain leather'.

Palygorskite consists of lath-like or fibrous crystals which tend to pack together in bundles and it is these bundles which make up the massive mineral. Due to relatively small bonding forces between individual palygorskite crystals mechanical separation into successively smaller fibres is possible. The mineral exhibits a considerable surface area of up to 240 m^2/gm. Palygorskite does not exhibit either the pronounced cation exchange capacity or swelling ability of the montmorillonite type minerals.

Individual aggregates of well oriented crystals often lie askew to each other, to give a "bundle of straw" effect. The spaces between individual aggregates become empty pores when the mineral is dried and thus available for absorption of liquids.

Palygorskite may be activated by thermal treatment to increase its adsorptive capacity. Commercial products are generally prepared to contain different amounts of volatile matter, namely water.

Typical physical properties of commercial palygorskite clays are shown in Table 2.

3. SORBENT APPLICATIONS

3.1 Absorbents

Products consisting of palygorskite, bentonite, diatomite, and a range of other materials, in both granular and powdered form are marketed in Australia for use as absorbents. The main markets are as an industrial oil or general spillage absorbent and the pet litter market. Although no accurate figures on the total usage of absorbent clays were available one indirect source stated that the industrial market (oil and spillage) could be 5-7 thousand tonnes per annum.

There are no recognised performance specifications for absorbents in Australia and both the properties and composition of products tested varied considerably. Further there are no current British or ASTM specifications governing the behaviour of absorbent materials although a USA Federal Specification P-A-1056A (Absorbent Material, Oil & Water for floors and decks) does outline their requirements for purchases by U.S. General Services Administration. The specification states that absorbent granules consist of a uniform mixture of minerals of the silicate type. They must be clean, uniform, and free of lumps or foreign matter, and no more than 10% of them can pass through an 80-mesh sieve in the attrition resistance test. (This test is made by shaking the granules with steel balls on a screen, according to a specified procedure). The size and absorbent characteristics required of the granules are given in Table 3.

Of six commercially available absorbent pet litters examined, only one, a product purchased some five years ago, contained relatively pure palygorskite and a second possibly contained a small amount. As expected the absorbancy values of the various products varies considerably and this together with the respective mineralogy is given in Table 4.

The absorbancy test was simple, consisting of soaking a known weight of each product in water for one hour followed by draining for half an hour on a 150 micrometre screen and reweighing. Absorbancy was calculated as a percentage of retained water to dry weight.

3.2 Pesticide Carriers

Many herbicides, pesticides and insecticides for certain dusting and spraying applications contain between one and twenty percent of active ingredient. The remaining eighty or more percent is a carrier diluent and other agents which permits the effective and economic application of the chemical. Materials used as carriers include palygorskite, sepiolite, bentonite, kaolin, diatomite, mica, talc, perlite, vermiculite and pumice. Each carrier material has desirable properties that vary in degree depending on the particular toxicant and the type of application for which the pesticide is to be used. If the pesticide is used as a dust and is required to adhere to foliage then bentonite may be highly effective or if it is required to fall to the soil then palygorskite or pumice may be satisfactory.

Both granular and fine powder forms of carrier diluents are used, again depending upon the application, and the properties of the carrier are often controlled by the country in which they are used. In the U.K. for example there are legal requirements, both under the Pharmacy and Poison Act and under the Agricultural Poisonous Substances Regulations, specifying that the particle size range of granular carriers used with toxic formulations shall give not more than 4% by weight passing through 60 mesh (BSS) and not more than 1% by weight less than 100 mesh (BSS). In Europe similar regulations apply. No regulations or specifications apply to the nature of carrier diluents used in pesticides in South Australia.

In Australia a number of companies are involved in pesticide manufacture the largest being I.C.I. Australia Ltd, Bayer Australia Ltd, Ciba-Geigy Australia Ltd and Roche-Maag.

Both bentonite and attapulgus clay (palygorskite) are used as carrier diluents in the formulation of dispersable insecticide powders. The total market for carrier diluents is approximately 3 000 tonnes per annum however this includes other types of carrier materials. Attapulgus clay represents only a few hundred tonnes of this total market although because of trends within the industry and the rising cost of petroleum products, zylene and toluene which are used in a range of emulsified sprays, utilization of dispersible powders may increase with a subsequent increase in demand for the clay carriers.

3.3 Wine Fining

Fining defines the method of clarifying or purifying liquids by adding a substance or substances in solution or suspension which, when added to the liquid react with the tannin, acid, protein or with some added substance to give heavy, quick settling coagulums. In the Australian wine industry bentonite is the most important material used for fining.

The choice of a material for wine treatment is dependent upon certain qualities which the material should possess. These are based on recommendations by Ribereau-Gayon and Peynaud (1961) :

a) Ability to remove proteins

Proteins in wine are normally positively charged and are absorbed by bentonite by charge neutralization

b) Ability to prevent copper casse

Although bentonite is ineffective in removing copper from wine, a good bentonite will prevent the formation of copper casse (haze in the wine) by effectively removing the protein in the wine which is necessary for copper casse formation

c) Ability to eliminate colour precipitation in red wines

d) Ability to effect mechanical clarification

Authorities within the wine industry state that natural sodium bentonites, both powdered and granular, are used almost exclusively for fining in Australia although some sodium exchanged calcium bentonites are available, mainly New Zealand bentonite, which have effected some limited market penetration.

Usage of bentonite for fining wine depends upon many factors including type of wine, age at bottling and the required result but estimates of the requirement may be 1.4 kgs per 4500 L (3 lbs/1000 gallons) for red wines and 4.5 kgs per 4500 L (10 lbs/1000 gallons) for white wines.

With the annual production of wine in Australia at 200 000 L and an average usage of 2.3 kgs per 4500 L an estimated market for bentonite of 102 tonne per annum is available.

Within South Australia the bulk of the market is supplied by a company marketing Volclay. A number of grades of the material is available which generally vary only in their physical characteristics, mainly dry sieve analysis. A general specification and data sheet prepared by the producers of Volclay (American Colloid Company) is reproduced as Appendix A.

An Italian producer of bentonite, Industria Chemica Carlo Laviosa SpA, market a product Enobent LCL for the wine industry. This is a granulated grade of bentonite with the following properties :

De-proteinizing power*	32 mg/L of total azote
Sodium soluble	1.3%
Soluble lead	absent
Arsenic	absent
Soluble phosphate (P_2O_5)	0.15%

*according to oenological international code.

3.4 Refining and Bleaching Edible Fats & Oils

Natural fuller's earths, activated clays, activated carbon and non bleaching filter aids are used extensively in the refining and bleaching of edible fats and oils both in Australia and overseas. A wide range of products are currently being imported to supply the industry and conform to the requirements of individual users.

Natural fuller's earths, in general, possess a lesser degree of decolourizing power (bleaching efficiency) than the acid activated clays and are consequently used in instances where minimal bleaching is required or the oils being bleached are sensitive.

Acid activated clays are produced in a range of active grades from neutral to slightly acid which assists selection of the best available material for the application. Neutral earths, like the natural earths, do not materially increase the free fatty acid content of the oils upon which they are used. However slightly acid grades, although stronger bleaching agents, are inclined to hydrolyse the oil slightly and increase its free acid content. Slightly acid grades are often more effective in removing chlorophyl in some soyabean oil than a neutral clay because of the instability of chlorophyl under acid conditions.

Acid activated earths retain more oil per unit weight of clay than do neutral earths although, due to their greater efficiency, their use generally leads to a lower over-all loss of oil through retention because of lesser quantities required. Less active fuller's earths may retain 20-25% of their own weight in oil whereas acid activated earths usually have a retention of 30-40% of oil.

Besides bleaching clays, the only adsorbent used to any extent on fatty oils is activated carbon but because of its high cost and oil retention it is not often used alone but blended with 10 to 20 parts of clay for bleaching some vegetable oils in specific applications. One of its main advantages over activated and natural clays is its effectiveness in removing "bloom" caused by traces of mineral oil in vegetable oils and for adsorbing traces of soap in refined oils. Soap is formed from the reaction of aqueous alkaline solutions on the free fatty acids in vegetable and animal oils and fats which is a common pretreatment procedure to bleaching.

The choice of an adsorbent depends in most cases upon factors which include cost, activity, degree of oil retention, particle sizing and filtration rate. A typical particle size distribution for bleaching earth used in the edible oil industry is given in Table 5. Although laboratory bleach tests and oil retention tests will give some indication of the value of a bleaching earth it is generally necessary to resort to testing on a larger scale under the specific conditions operating in a plant, which may be considering purchasing the material, to accurately evaluate its usefulness.

The amount of adsorbent required for any bleaching operation, in a specific plant, will vary depending upon many factors including the nature and activity of the adsorbent, the variety of material (oil, fat or grease)to be bleached and the colour of the unbleached product and of the desired end product. Bailey (1951) states that the amountsof bleaching clay used vary from about 0.25% for lard to about 5% for dark-coloured inedible tallows and greases. Australian producers of edible fats and oil have indicated usage of 1-2% of high grade bleaching earth for bleaching of palm, sunflower, cotton-seed and safflower oils although one refiner of rape, sunflower, soyabean, linseed and peanut oil indicated a maximum usage of 1%.

Overseas producers of natural and acid activated earths include companies such as Sud-Chemie A.G., LaPorte Industries Ltd, Union Carbide, Erbsloh & Co and Minas de Gador (Spain). Products from all of these manufacturers, with the possible exception of Minas de Gador, are available in Australia in conjunction with numerous others including earths from Japan and India. With possible minor exceptions all of the bleaching earth used in Australia is imported.

Sud-Chemie A.G. supply bleaching earths in a range of grades, as do the majority of the producers, for different applications. Specific details of each grade were not obtainable but a general indication of suitability and range of applications for each grade is shown in Table 6.

The total edible oil and fat market in Australia is estimated at 180 000 tonnes per annum and on the basis of an average earth on oil usage of 1.2%, the total market for bleaching earth, both natural and activated is about 2 200 tonnes per annum.

Sepiolite has been found to possess high bleaching activity for cottonseed oil (Dandy 1967) although lower filtration rates and high oil retention were notable in comparison with a commercially available fuller's earth.

Anna 'Kaolin', a refractory material consisting of kaolinite and anauxite mined in Illinois, U.S.A., was investigated over 40 years ago as a bleaching earth for edible and mineral oils with excellent results compared with an English fuller's earth XL available at that time (Piersol et al 1933). In general, although lower filtration rates and a slight increase in oil retention were recorded for Anna 'Kaolin' when bleaching cottonseed oil, bleached products were at least comparable. Both material and usage rates for the kaolin were slightly less than for the fuller's earth product.

Test methods for evaluating bleaching earth efficiency for soy-bean and cottonseed oils are outlined in the American Oil Chemists Society A.O.C.S. Official Method Cc 8b-52, revised April 1952, (see Appendices B & C). & A.O.C.S. Official Method CC 8a-52 corrected 1958 (Appendix D). These tests relate to the comparison of a material being tested with an official natural bleaching earth approved by the American Oil Chemists Society and relate to colour determinations of the bleached oils and oil bleached by the official earth in the same test. Piersol (1933) and Bailey (1951) define other tests which may be used, particularly for comparative evaluations. However, since all of the literature reviewed indicates that there is generally disagreement between the laboratory and commercial results obtained it would seem that, as is common practice, the testing of a bleaching earth is best undertaken by the user industry.

3.5 Pharmaceutical Uses

Clays, and in particular kaolins, are commonly used as adsorptive agents in intestinal suspensions. In the mid 1950's activated attapulgite (palygorskite) was first used in therapeutics as an adsorbent for alkaloids, bacteria and toxins and according to Barr (1958) its adsorbing properties were found to be far superior to those of kaolins formerly used in similar preparations.

Activated attapulgite is a heat treated product containing different amounts of volatile matter, namely water. Various products are available which depend upon their specific thermal treatment and the products of one American producer, Minerals and Chemicals Corporation of America, are shown below :

		Ignition Loss	Colour
Attasorb®	LVM	6% at 1800°F	Light cream
Attasorb	RVM	9% at 1800°F	Light cream
Attasorb	HVM	19% at 1800°F	Light cream

The interstinal adsorbent preparations are believed to combat intestinal irritation by (a) adsorbing toxins and bacteria which are thought to be responsible for the onset of diarrhoea, vomiting, nausea and cramps in various types of intestinal infections and (b) coating the inflamed mucous membrane of the tract.

Activated attapulgite has two important properties which are superior to those of kaolin. Firstly it has been shown to be 5 to 8 times more efficient as an adsorbent for bacteria and toxin than kaolin and secondly it has superior absorptive properties compared to kaolin and in intestinal preparations this leads to more effective absorption of the aqueous part of inflammatory secretions which thus aids in stool formation.

3.6 Textile Industry

During the nineteenth and first half of the twentieth century fuller's earth was widely used for the removal of grease and dirt from raw wool. However, with developing technology more effective methods were implemented and present general practice is believed to involve solvent extraction and chemical bleaching processes.

Sources within the industry state that no fuller's earths are now used in Australia for cleaning wool although there may be some application for them overseas for wool grease refining.

3.7 Other Industries Using Bleaching Earths

Bleaching earths are used by soap and chemical manufacturers and in areas of the food industry in addition to edible oil refining and bleaching.

Australia consumes approximately 35 000 tonnes of tallow annually for soap manufacture and 20 000 tonnes per annum for chemicals and the bleaching earth market for these industries is estimated at approximately 2 000 tonnes.

In general bleaching earths used for edible oils are similar to those used to bleach tallows for soap and chemical manufacture. A.O.C.S. Official Method CC 8d-55 "Refined & Bleached Colour" is the accepted standard method used in the soap industry for evaluating the colour of a sample after treatment with a bleaching earth. The method is reproduced as Appendix E.

4. PRODUCTION AND IMPORT STATISTICS

Statistics published in the Australian Mineral Industry Review and Australian Mineral Industry Quarterly provide data related to the production and value of bentonite, bentonitic clay and fuller's earth in Australia, and the imports of bentonite and activated natural mineral products and clays. Unfortunately imports of fuller's earths are not recorded separately.

Fluctuations in bentonite production and imports since 1970, as shown in Tables 7 and 8, mainly reflect activity in oil drilling, foundry demand and iron ore pelletizing in Tasmania and Western Australia. Only a very small proportion of the cumulative bentonite figures, possibly five percent, may be attributed to uses other than the three major ones mentioned and it is estimated that a maximum of two percent is used as a sorbent medium. From Tables 6 and 7 this estimate would place the sorbent market for bentonite at less than 700 tonnes in 1976. As indicated under the discussion of Absorbents a larger absorbent market exists but alternative materials are commonly used.

The bulk of Australian production of fuller's earth is mined at Dubbo, N.S.W., and virtually all of the production would be used in bleaching applications in conjunction with the imported activated natural mineral products and clays (see Table 9). Imports of palygorskite (attapulgite) would be included in the available figures, as are other activated materials, for example carbon, but since the various materials are not differentiated it has not been possible to obtain definite consumption data for activated bentonites, fuller's earths or palygorskite. However, the figures do indicate a maximum market of nearly 4000 tonnes, in 1977, for activated products including clays the majority of which would have been used in oil refining and bleaching processes.

Thus, from the available data it is concluded that the present Australian market for bentonite and palygorskite as sorbent material is small, possibly less than 4 500 tonne most of which is for activated bentonite imported for oil bleaching and clarification.

5. SUMMARY AND CONCLUSIONS

The utilization of bentonitic clays and the hormites (palygorskite and sepiolite) as sorptive minerals either in their natural or activated state within Australia is not extensive.

In the wine industry imported natural sodium bentonites are used as fining agents but only minimal tonnages, between 100 and 150 tonnes per annum, are consumed and growth of this market, if any, will be small in the foreseeable future.

For the bleaching of edible, and some inedible, oils and fats activated clays are predominantly used although some natural fuller's earths in small tonnages are consumed. This market appears to be in the vicinity of 4 000 tonnes per annum.

The absorbent material market may be a significant one but no useful figures were obtained to estimate the actual tonnages consumed in industry as absorbents for oil spills in factories or in the home, laboratories or animal centres as a pet litter.

As shown by the analysis of some commercially available pet litters virtually any clay or material capable of absorbing moisture is acceptable. Due to the manner in which these products are used a highly absorbent material is not necessarily required since it would generally be discarded well prior to saturation.

Carrier diluents for dispersable pesticides include bentonite and palygorskite (attapulgus clay) in Australia and although a total market of 3 000 tonnes is estimated to exist only a proportion is known to be currently supplied by the minerals in question. The diluents are imported, mainly from the United States.

6. PALYGORSKITE SAMPLES FROM THE LAKE FROME AREA

6.1. Introduction

Samples of magnesium-rich clay from the Lake Frome area of South Australia have been examined to determine their suitability as general absorbents. Previous work related to these clays indicated that of eight samples investigated from the Lake Millyera, Jadliaura Creek and Lake Tarkarooloo areas six samples contained palygorskite in association with quartz and, generally, halite. A high proportion of calcium sulphate in the form of gypsum and bassainite was detected in one sample from Lake Millyera which also contained palygorskite. A complete mineralogical and chemical analysis of the six samples containing palygorskite is given in Tables 10 and 11. Although not detected by X-ray diffraction it is probable that some of the materials also contain some jarosite type mineral as indicated by the chemical analysis and colour changes on heating to 650°C. A discussion of the materials is given in Amdel Report 1/1/100, March 1978.

Amdel Report MD 1462/78 refers to preliminary absorption tests on calcined (650°C for 2 hours) and screened (-5+1 mm) samples obtained from each material. The results indicated that those materials highest in palygorskite content showed the highest water absorbancy values. Overall, however, the results obtained were fairly poor when compared with the absorbancy of a commercially available palygorskite product sold as a pet litter absorbent material.

The work reported herein relates to the investigation of a wider range of pet litters and materials including diatomite, bauxite and magnesite, all commercially available for absorbent applications. The absorbancy of these products is compared with the absorbancy of the best materials from the Lake Frome area available for study after calcination at 650°C for 2 hours and in the case the material containing the highest percentage of palygorskite, at various calcination temperatures.

6.2 Materials Examined

Commercial Pet Litters	Amdel No.	Composition
Tydee Tom (Old Product)	CE 5269	Palygorskite
Embassy Brand (Old Product)	CE 5270	Illite
Embassy Brand (Current Product)	CE 5273	Palygorskite or Illite with Mullite
Woolworths Brand	CE 5274	Calcined Bauxite
Kitty Litter - Trade Name	CE 5275	Magnesium Oxide

Commercial Absorbent		
Floor-Dry 85 (Eagle Pitcher)	CE 5313	Diatomite

Lake Frome Materials	Clay Register No.	Composition
Lake Millyera 2A	R696A	Refer Table 10
Lake Millyera 2B	R696B	Refer Table 10
Lake Millyera 4 (Selected)	R697	Refer Table 10
Lake Millyera (Representative)	R698	Refer Table 10
Jadliaura Creek	R699	Refer Table 10

6.3 Assessment Procedures

The size distribution of all material examined was determined using a set of screens ranging from 4 000 micrometres to 250 micrometres (4-60 mesh B.S. 410). The commercial materials were screened as received and the percent retained on each screen is shown in Table 12. The Lake Frome materials were calcined at 650°C for 2 hours, crushed and screened prior to absorbancy evaluation and the material from Jadliaura Creek was calcined at additional temperatures (400°C, 500°C, 600°C and 700°C) prior to evaluation. The material from this area contains the highest proportion of palygorskite and as previous results have indicated it shows superior absorbing properties after a 650°C calcination compared with the remaining material available for testing from the Lake Frome area. The range of temperatures were thus selected for this sample to optimize, by calcination, the absorption capacity of the material. All materials were approximately minus 6 millimetres prior to calcination.

The absorbancy test consisted of immersing a known weight of material in water for 2 minutes followed by removal of excess water from the sample by suction filtering on a Whatman No. 1 (medium fast) filter paper for 4 minutes. The sample is at this stage in a saturated but surface dry condition. The saturated samples were reweighed and the water absorbance of the material calculated. The tests were undertaken on material which contained some moisture, governed by atmospheric conditions, and the result corrected on an original dry material basis after determination of the natural state moisture condition of each material. Results expressed as millilitres of water absorbed per gram of dry material are given in Table 12.

6.4 Results and Discussion

Since there are neither recognized performance specifications nor test procedures for absorbents in Australia and further no current British or ASTM specifications governing their behaviour exist, the results obtained and the absorbancy test procedures used during this investigation are for comparative purposes only to classify the materials according to absorbancy efficiency. Reference is however made to a U.S. Federal Specification for general information.

Of the commercially available materials tested the older Embassy Brand pet litter product (CE 5270), which is composed of illite, and the currently available Floor-Dry product from Eagle Pitcher, a diatomite, have the highest absorbancy efficiency. In terms of the USA Federal Specification P-A-1056A (Absorbent Material, oil and water, for floors and decks) neither material attains the minimum absorptive capacity of 0.9 mL per gram of sample required by the specification under the imposed test conditions. The required characteristics of absorbent granules according to this specification are shown in Table 3.

The only material examined to satisfy the grading characteristics of this specification is Tydee Tom pet litter.

Of the remaining commercial products examined Tydee Tom and the current Embassy brand pet litters, the former a palygorskite and the latter either palygorskite or illite (poorly defined material), have comparable absorbancy efficiencies and would perform relatively satisfactorily as general absorbents. The Woolworths brand product, a calcined bauxite, has the capacity to absorb approximately 50% of its weight of water which is possibly adequate for the general pet litter market. Kitty Litter however is relatively ineffective and inefficient as an absorbent material for any but the lightest applications.

After calcining at 650°C the material from Jadliaura Creek performs satisfactorily as a low grade absorbent product and would be generally comparable in efficiency to the pet litter products examined. In this regard therefore it could be considered as a potentially competitive material although its absorbancy falls well below that of a high grade product.

The efficiency of this material appears to increase with calcination temperature up to 650°C. At 400°C the material lacks granular strength and may breakdown during transport and in some applications, during use. Calcination at 500°C produces a material of adequate strength but lower absorbancy efficiency than higher temperature calcination up to 650°C. At 700°C the absorbancy efficiency of the material decreases. With increasing calcination temperatures the material changes from a buff tan colour at 400°C through a pinkish brown at 500°C to red at 600°C and above. Colour and possibly staining from the material may be factors which could affect the marketability of the material.

Of the remaining samples examined all with the exception of the Lake Millyera R696B material should be suitable, after calcination, for the pet litter and general low duty industrial market.

6.5 Conclusion

For general applications, mainly the pet litter and industrial low duty absorbancy market, the majority of the materials examined from the Lake Frome area, after calcination at 600°C to 650°C, would be comparable to products similar to those tested herein in terms of absorbancy efficiency. Colour however may well be a detracting feature of the material and this aspect requires consideration.

In comparison with a good quality absorbent material which would absorb at least its own weight of liquid, the Lake Frome materials thus far examined are inferior. Within the near future it is believed that a high grade palygorskite from W. Australia may be available to the market.

7. REFERENCES

BAILEY, A.E., 1951. Ind. Oil & Fat Products. Interscience Publications, 2nd Ed. N. York.

BARR, M., 1958. Activated Attapulgite. Pract. Pharmacy Ed. 19(2).

BOTTRILL, R.D., & SPENCER,W.G. 1978. Palygorskite - Structure and Properties. Amdel Report 1/1/210, Progress Report No. 1.

DANDY, A.J., 1967. The Bleaching or Cottonseed Oil by Sepiolite. E. African Agri. & Forestry J. Jan.

DAY, L.J. 1978. Bentonite - Structure Properties and Uses. Amdel Report 1/1/210, Progress Report No. 2.

GRIM, R.E., 1972. Int. Clay. Conf. (AIPEA).

JONES, G.K. 1972. Fuller's Earths - Active Clay Minerals.

JONES, G.K. 1974. Catalyst & Adsorbent Uses for Industrial Minerals. Proc. First Ind. Mins Int. Congress.

KNIGHT, W.C. 1898. Bentonite. Eng. Min. J., 66:491.

PIERSOL, R.J. et al. 1933. Anna 'Kaolin' as a New Decolorizing Agent for Edible Oils. State of Illinois - State Geol. Surv. RI 27.

ROSS, C.S. & SHANNON, E.V. 1926. Minerals of bentonite and related clays and their physical properties. J. Am. Ceram. Sci., 9:77-96.

WRIGHT, P.C. 1968. Meandu Creek bentonite - a reply. J. Geol. Soc. Aust., 15:347-350.

APPENDIX A

Volclay

PHYSICAL ARACTERISTICS OF VOLCLAY BENTONITE

properties of Volclay are those of montmorillonite, a ineral of unique characteristics, which constitutes of Volclay substance. Montmorillonite has the ap- nate chemical formula:

$[(Al, Fe)_{1.67}Mg_{0.33}]\,Si_4O_{10}(OH)_2(Na, Ca_{0.33})$

other 10 % consists of minute fragments of other ls, the most abundant being feldspar. There are fractions of gypsum, calcium carbonate, and quartz aces of partially altered volcanic glass, biotite mica, tite, limonite, hematite, leucoxene, apatite, zircon, titanite, and tremolite.

AL CHEMICAL ANALYSIS, MOISTURE FREE BASIS

	Percent by Wt. (Varies Between)	
SiO_2)	58.0	64.0
na (Al_2O_3)	18.0	21.0
Oxide (Fe_2O_3)	2.5	2.8
sia (MgO)	2.5	3.2
aO)	0.1	1.0
Na_2O)	1.5	2.7
(K_2O)	0.2	0.4
Oxide (FeO)	0.2	0.4
m Oxide (TiO_2)	0.1	0.2
minor constituents	0.5	0.8
ally-held water (H_2O)		5.64
nically-held water (H_2O)		0.00

PARTICLE SIZE

n dispersed in water, Volclay separates into ex- fine particles, as follows:

% to 97 % finer than 44 microns (No. 325 Standard U.S. Sieve)
% to 94 % finer than 5 microns
% to 89 % finer than 0.5 micron
% to 65 % finer than 0.1 micron

micron is about 1/25,000 inch. One cubic inch of lay, when disintegrated in water, is estimated to 00 billion individual flakes, and the total surface these particles is about one acre in extent.

GENERAL

ic gravity—2.7. Actual weight relative to volume on the degree of pulverization, the packing and of the sample.

lue of water suspensions is 8.5 to 10.0.

of refraction—1.55.

Hardness—1 to 1.5. Slightly harder than talc.

BASE EXCHANGE

Volclay is noted for its base exchange properties; in a water solution, it gives up sodium and potassium ions and takes in calcium and magnesium ions, thus softening the water slightly. It also enters strongly into base exchange with organic bases, extracting them from solutions of their salts.

The exchangeable metallic bases of average Volclay, determined quantitatively by leaching with ammonium acetate are:

ELEMENT	meg./100 gms.
Sodium	60 to 65
Calcium	15 to 20
Magnesium	5 to 10
Potassium	1 to 5
Sum-corrected for sulphates	85 to 90

Because the exchange ions are affected by many factors, values are somewhat different in different shipments. These values are not guaranteed to exist in any lot or any one shipment.

SWELLING

The rate of swelling depends upon the fineness, grade and on how the bentonite is handled; all grades expand very slowly when water is poured on them, much faster when they are poured into water. Finely powdered Volclay grades absorb water slowly; MX-80 Volclay absorbs it intermediate and specially sized KWK Volclay absorbs water more rapidly.

Volclay absorbs nearly 5 times its weight of water and at full saturation it occupies a volume 12 to 15 times its dry bulk. On drying, it shrinks to its original volume. The swelling is reversible — it can be wetted (swelled) and dried (shrunk) an infinite number of times, if the water used is fairly pure.

It absorbs and swells faster in hot water than cold; it does not swell in alcohol, gasoline and similar liquids; it swells only slightly in solutions of strong chemicals, such as acids, alkalies or salts.

WATER SUSPENSIONS

When mixed with 7 to 10 parts water, it makes gelatinous pastes. With 15 to 20 parts water, it forms milky, flowable sols.

Figures are given showing the consistency (viscosity) of two Volclay suspensions compared with clear water, mixed thoroughly:

	Centipoises
Clear Water	1
5% Volclay (1 Part Volclay to 19 Parts Water)	3 to 8
6-1/4% Volclay (1 Part Volclay to 15 Parts Water)	8 to 25

The sols were tested immediately after stirring; they ow higher readings after standing a few hours.

In thinner dilutions — as 1 part Volclay to 99 distilled ater — most of the Volclay remains suspended indefiely. Even in dilutions as low as 1 to 5000, a considerable rt does not settle. Distilled water must be used with low lclay concentrations as the electrolytes in tap water ght cause partial flocculation.

Dilute suspensions show Brownian movement — the rticles are in motion, colliding and repulsing each other. vier slurries exhibit thixotropy, a kind of gelation that urs when they stand quiescent, but which reverts to idity on being shaken or stirred.

EFFECT OF ELECTROLYTES

rticles of Volclay in water carry strong negative charges, using them to attract and cling to positively charged parles of matter. When neutralized by oppositely charged bstances, they floc together, forming spongelike aggretes, and if this occurs in dilute dispersions, the flocs set. In thicker mixtures, however, as those containing 6% more of Volclay, the effect of added electrolytes is to rease the viscosity.

spensions of Volclay are ordinarily difficult to filter, ming impenetrable cakes which seal off water. One of effects of neutralizing or flocculating the particles is to ke such suspensions more readily filterable.

ollows that all dispersions of Volclay are profoundly ected by electrolytes. The higher the valance of the latthe stronger the effect; monovalent cations are mildly ive in causing flocculation, di-valent ones more so and alent ones much more so.

order of adding electrolytes is important. If an electrois added to a thick slurry in which the Volclay has first n fully hydrated and swelled, the consistency of the ry will be increased; but if the water is first treated with electrolyte and the Volclay put in later, the dispersion be thinner than a mixture of Volclay and clear water.

perature of water and time of standing also are fac. Some electrolytes stiffen the slurries temporarily, followed by thinning, after standing days or weeks; others reverse this action.

SORPTION

Montmorillonite unit cells, of the particular kind that constitute Volclay, have the outstanding peculiarity of expanding accordion-like in water. This enlarges the space between the sheets which form the structure and permits the free ingress and egress of ions of various kinds.

The mobility of the flakes when in suspension brings them in close contact with other dissolved and suspended substances. Particles of matter are not only adsorbed onto the surface of the bentonite molecule, but probably also absorbed within its lattice-like structure. The avid sorption of Volclay for other substances — both organic and inorganic — is therefore due to one or more of these factors: great surface area; spongy structure; mobility; base-exchange; strong negative polarity.

BOND STRENGTH

The maximum adherent powers of Volclay in moistened masses with other minerals is exerted when the added moisture is 50% of the weight of the Volclay.

EFFECT OF TEMPERATURE

The properties of Volclay are unaltered at temperatures below 204° C. The chemically held water is progressively driven off when exposed to higher heats for any length of time and is completely gone at 660° C. However, if heated to 537° C. and quickly cooled, its properties are unchanged.

Its swelling properties decrease progressively in the same ratio as the loss of chemically held water.

Softening begins about 1037° C. and fusion occurs at 1337° C.

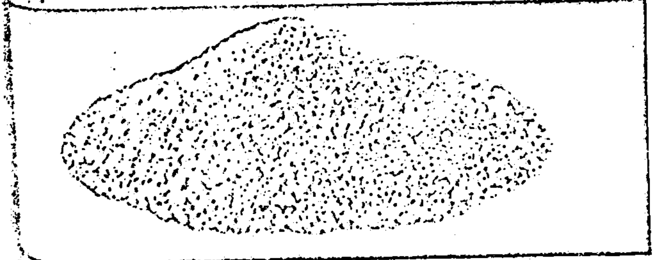
Volclay imparts to masses of other minerals bonded with it an extraordinary "hot strength", i.e., resistance to load pressure while hot. In the range of temperatures just below the softening point, its "hot strength" far exceeds that of other clays.

MECHANICALLY HELD MOISTURE

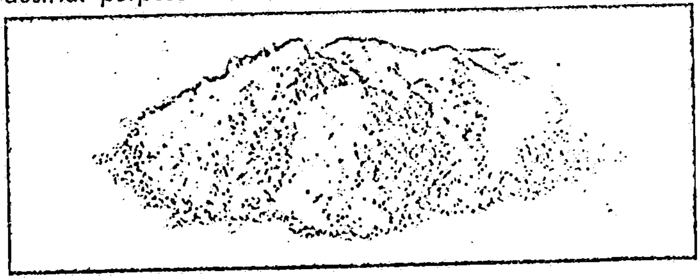
Volclay as shipped contains different moisture contents. When exposed to the atmosphere, it slowly gains or loses moisture according to the humidity.

It requires 2 hours at 105° C. to 110° C. to dry it to a moisture-free condition.

KVOLCLAY — *fine pellet-size bentonite. Disperses in water quicker than powder and yields the same, smooth gel.*



SPV VOLCLAY — *powdered bentonite. Mainly for general industrial purposes where bentonite is not mixed with water.*



APPENDIX B

Bleaching Test for Soybean Oil

SAMPLING AND ANALYSIS OF COMMERCIAL FATS AND OILS

A.O.C.S. Official Method Cc 8b-52

Formerly Cc 8b-49
Revised 1949, 1952, and 1955
Revised 1956
Reapproved 1973

Bleaching Test

Definition: This method determines the color of the sample after treatment with a specified bleaching earth under conditions of this test

Scope: Applicable to refined soybean oil.

A. Apparatus and Supplies:

1. As prescribed in A.O.C.S. Official Method Cc 8a-52, Section A, paragraphs 1 to 9, inclusive.
2. Official Activated Bleaching Earth tested and approved by the designated Committee of the American Oil Chemists' Society. A fresh supply must be obtained from the Office of the Secretary of the Society, 508 South Sixth St., Champaign, Illinois 61820, August 1, of each year.

B. Procedure:

a. *For Normal Colored Oils*

1. Filter the oil as directed in A.O.C.S. Official Method Ca 9a-52, Section E, paragraph 11. Eaton and Dikeman No. 617 or Reeve-Angel No. 230 filter papers may be used to filter the refined oil for use in running the bleach test. The purpose is to speed up the filtering rate. The use of these two "fast" filter papers is not permitted when the refined oil sample is to be used directly for color determination.
2. Weigh 300 g. of sample into the refining cup. Add official Natural Bleaching Earth in the amount specified on the label of the can.
3. Commence stirring at 250 ± 10 r.p.m. and heat immediately to 120°C. ± 2°, requiring 5 minutes ± 1 minute. Continue stirring at the same rate for 5 minutes. Do not allow the temperature of sample to drop below 115°C. during this period even if reheating is necessary.
4. Promptly pour all the oil and earth into a dry filter paper. Allow a minimum of 60 ml. of oil to pass. Then collect a sufficient amount for the color reading.
5. Determine the color as directed in A.O.C.S. Method Cc 13b-45 or Method Cc 13c-50.

b. *For Green Oils—High Chlorophyll Content*

1. The procedure is identical with that described in (a) except that 4% (12.0 g.) of the Official Activated Bleaching Earth is used instead of Natural Earth.

APPENDIX C

Modified Bleach Test for Soybean Oil

A.O.C.S. Official Method Cc 8a-63
Revised 1963
Reapproved 1973

Modified Bleach Test for Soybean Oil

Reagents and Apparatus:

Same as in A.O.C.S. Official Methods Ca 9a-52, Cc 8b-52, Ca 5a-40.

Operation:

Determine the free fatty acid in the oil as in A.O.C.S. Method Ca 5a-40. Refine 500 grams of the sample as follows. Place the sample in the refining machine at 20 to 24° C. and start agitation at 250 rpm. Add lye as specified in Ca 9a-52 for soybean oil and the free fatty acid, using the highest dosage of the maximum lye (see Table I below). Agitate for 15 minutes. Decrease the speed to 70 ± 5 rpm, heat to 65° C., and agitate for 15 minutes at 65° C. Allow the oil to stand at 60–65° C. for at least one hour to settle the foots. Longer settling periods may be used, but normally no longer than two hours should be required.

Remove from the machine and decant the clear oil into a second refining cup, being careful to exclude any free foots. Filter the decanted oil through an approved paper and bleach as outlined in Cc 8b-52.

TABLE I
Weight of Lye in Grams per 100 Grams of Oil

FFA	12° Max.	FFA	12° Max.	FFA	12° Max.	FFA	12° Max.
.1	7.0	1.4	10.1	2.7	13.2	4.0	16.4
.2	7.2	1.5	10.4	2.8	13.5	4.1	16.6
.3	7.5	1.6	10.6	2.9	13.7	4.2	16.8
.4	7.7	1.7	10.8	3.0	14.0	4.3	17.1
.5	8.0	1.8	11.1	3.1	14.2	4.4	17.3
.6	8.2	1.9	11.3	3.2	14.4	4.5	17.6
.7	8.4	2.0	11.6	3.3	14.7	4.6	17.8
.8	8.7	2.1	11.8	3.4	14.9	4.7	18.0
.9	8.9	2.2	12.0	3.5	15.2	4.8	18.3
1.0	9.2	2.3	12.3	3.6	15.4	4.9	18.5
1.1	9.4	2.4	12.5	3.7	15.6	5.0	18.8
1.2	9.6	2.5	12.8	3.8	15.9		
1.3	9.9	2.6	13.0	3.9	16.1		

APPENDIX D

Bleaching Test for Cottonseed Oil

SAMPLING AND ANALYSIS OF COMMERCIAL FATS AND OILS

A.O.C.S. Official Method Cc 8a-52

Formerly Cc 8a-47
Revised 1949, 1952, and 1955
Corrected 1958
Reapproved 1973
Corrected 1977

Bleaching Test

Definition: This method determines the color of the sample after treatment with a specified bleaching earth under the conditions of this test.

Scope: Applicable to refined cottonseed oil.

A. Apparatus and Supplies:

1. Balances
   - a. For the oil, torsion type or equivalent, capacity 1000 g. and sensitive to 0.1 g.
   - b. For the clay, balance sensitive to .05 g.
2. Balance weights, .01 g to 500 g.
3. Refining cups, stainless steel or unchipped enameled iron, seamless, with handle, 4 to 4.5 inches in diameter, 4 to 4.5 inches deep, total capacity ca 900 ml.
4. Bleaching apparatus, which may be similar in design and construction to the Refining Apparatus (A.O.C.S. Official Method Ca 9a-52). The essential features of the bleaching apparatus are:
   - a. T-shaped paddles constructed of stainless steel, with 0.5 x 3.5 inch blade. The blade must be fitted to the shaft in such a way that oil or grime cannot accumulate in a crack or space between the two parts.
   - b. The paddles are driven at 250 ± 10 r.p.m. by any convenient means.
   - c. A heat source is required which will permit heating the samples to 120° C. in 5 minutes ± 1 minute and maintain them at not less than 115° C. Gas heat is recommended.
   - d. The support for the cups must be so arranged that they will not rotate or change position during the test, and the agitator shaft must be centered, with the bottom of paddle at a distance of ¼ inch above the bottom of the cup. The design of this support shall also be such that the area at which heat is applied is essentially the entire bottom surface of the cup. The concentration of intense heat within small portions of this area must be avoided.
   - e. Thermometer clamps arranged so that a thermometer is held rigidly with the bulb completely immersed in the oil while agitating, but without interfering with the motion of the paddle.
5. Official Natural Bleaching Earth tested and approved by the designated Committee of the American Oil Chemists' Society. A fresh supply must be obtained from the Office of the Secretary of the Society, 508 South Sixth St., Champaign, Illinois 61820, August 1, of each year.

Bleaching Test

6. Filter paper, 32 cm. (12½ inch), E & D No. 513, Reeve-Angel No. 871, Whatman No. 2V, or S & S No. 596. Folded filter papers are optional.

   Eaton and Dikeman No. 617 or Reeve-Angel No. 230 filter papers may be used to filter the refined oil for use in running the bleach test. The purpose is to speed up the filtering rate. The use of these two "fast" filter papers is not permitted when the refined oil sample is to be used directly for color determination.

7. Colorimeter, color glasses, and color tubes as specified in A.O.C.S. Official Method Cc 13b-45 or spectrophotometer specified in Method Cc 13c-50.

8. Laboratory thermometer, 0 to 150° C., calibrated for 3 in. immersion.

9. Funnels. Stemless and seamless, of aluminum, stainless steel, or gloss (60° cone with 5 to 6″ top diameter and ⅜ to ½″ hole).

   Note: Corning catalog No. 6240 glass funnel, 6 in. diameter, specified when ordering, meets these requirements.

B. Procedure:

1. Filter the oil as directed in A.O.C.S. Official Method Ca 9a-52, Section 1, paragraph 11.

   Eaton and Dikeman No. 617 or Reeve-Angel No. 230 filter papers may be used to filter the refined oil for use in running the bleach test. The purpose is to speed up the filtering rate. The use of these two "fast" filter papers is not permitted when the refined oil sample is to be used directly for color determination.

2. Weigh 300 g. of sample into the refining cup. Add official Natural Bleaching Earth in the amount specified on the label of the can.

3. Commence stirring at 250 ± 10 r.p.m. and heat immediately to 120° C. ± 2°, requiring 5 minutes ± 1 minute. Continue stirring at the same rate for 5 minutes. Do not allow the temperature of sample to drop below 115° C. during this period even if reheating is necessary.

4. Promptly pour all the oil and earth onto a dry filter paper. Allow a minimum of 60 ml. of oil to pass. Then collect a sufficient amount for the color reading.

5. Determine the color as directed in A.O.C.S. Method Cc 13b-45 or Method Cc 13c-50.

APPENDIX E

Refined and Bleached Color for Soap Tallows and Greases

SAMPLING AND ANALYSIS OF COMMERCIAL FATS AND OILS

A.O.C.S. Official Method Cc 8d-55

Formerly Cc 8d-53
Corrected 1958
Reapproved 1973
Corrected 1977

Refined and Bleached Color

Definition: This method determines the color of the sample after treatment with alkali and a specified bleaching earth.

Scope: Applicable to tallows and greases intended for soap production.

A. Apparatus and Supplies:

1. Refining apparatus and supplies as described in A.O.C.S. Official Method Ca 9a-52, paragraphs 1 to 4, inclusive.
2. Bleaching apparatus, which may be similar in design and construction to the Refining Apparatus (A.O.C.S. Official Method Ca 9a-52). The essential features of the bleaching apparatus are:
   - a. T-shaped paddles constructed of stainless steel, nickel plated copper or brass (heavily coated) with 0.5 x 3.5 inch blade set at right angles to the shaft of the paddle.
   - b. The paddles are driven at 250 ± 10 r.p.m. by any convenient means.
   - c. A heat source is required which will permit heating the samples to 110°C. in not more than 5 minutes and maintaining them at not less than 105°C. Either gas or electrical heat is satisfactory.

   Note: If enameled cups are used they must be unchipped on the inside.
3. Official Activated Bleaching Earth tested and approved by the designated committee of the American Oil Chemists' Society. A fresh supply must be obtained from the Office of the Secretary of the Society, August 1, of each year.
4. Filter paper, Eaton & Dikeman No. 617 or Reeve-Angel No. 230, 250 mm. (10 inch).
5. Filter paper, 250 mm. (10 inch) such as E & D No. 513, Reeve-Angel No. 871, Whatman No. 2V or S. & S. No. 596.
6. Colorimeter, color glasses and color tubes as described in A.O.C.S. Official Method Cc 13b-45.
7. Hot water funnel or other suitable funnel heater adjusted to a temperature such that the sample will remain completely liquid during filtration, but not higher than 25°C. above the melting point.
8. Funnels, 125 or 150 mm. diameter.
9. Laboratory thermometer, 0 to 150°C.

B. Solutions:

1. Sodium hydroxide soln., 0.25 *N*, accurately standardized.
2. Sodium hydroxide, 20° Bé, (14.07 to 14.65% actual NaOH by weight) prepared as directed in A.O.C.S. Official Method Ca 9a-52, B, 3.

Refined and Bleached Color

3. Specially denatured alcohol, U.S.S.D. Formula No. 30 or 3A. Add 0.05% phenolphthalein and a sufficient amount of NaOH solution to give the alcohol a faint pink color. The alcohol must be faintly pink just before using.

C. Preparation of Sample:

1. Melt the sample if it is not completely liquid and shake or stir thoroughly to obtain a uniform mixture. Avoid local over-heating and do not heat more than 20° C. above the melting point.

D. Determination of Free Fatty Acids:

1. Weight 7.05 g. of well mixed sample into 115-ml. (4 oz.) oil sample bottle or 250-ml. Erlenmeyer flask and add 50 ml. of neutral alcohol containing 0.05% phenolphthalein.
2. Warm in a water bath and titrate with 0.25 *N* NaOH soln. until a permanent pink color is obtained, which persists after 30 seconds of vigorous shaking.
3. Free fatty acids as oleic, % = ml. of 0.25 *N* NaOH soln. used.

E. Procedure:

1. Weigh 500 g. of sample into a refining cup. Place in the refining machine, fill the water bath to the specified height (A.O.C.S. Official Method Ca 9a-52) and heat to 51° to 55° C.
2. Find the % excess NaOH in Table 1 corresponding to the % F.F.A. determined. With these 2 values substitute in the formulae to determine the amount of alkali soln. to use.
3. Start stirring at 250 r.p.m. and add the specified amount of 20° Bé alkali soln. as calculated in paragraph 2 and continue agitation after addition of the alkali for 5 minutes.

TABLE 1

% F.F.A. in fat	% Excess NaOH required
0.1 – 4.00	0.2
4.01– 6.00	0.3
6.01– 8.00	0.5
8.01–15.00	0.6

$$\frac{\%\ \text{F.F.A. in fat}}{7.05} = \%\ \text{NaOH to neutralize free fatty acids} = \text{A.}$$

$$\frac{5 \times (\text{A} + \%\ \text{excess NaOH required from table above})}{0.1436} = \text{grams of}$$

20° Bé soln. to add to 500 g. of sample.

4. Change the speed of stirring to 70 r.p.m. and increase the bath temperature immeditely to 61° to 64° C. Stir under these conditions for 10 to 15 minutes. It may sometimes be necessary to add a small

Refined and Bleached Color

amount of water to the mixture of tallow and foots to hasten coagulation and insure complete precipitation.

5. When the foots appear to be ready to settle, discontinue stirring and allow to stand until the foots have settled and the fat is clear. The condition of the foots can be determined by removing a small portion of the mixture from the cup with a teaspoon and observing the tendency to settle.

6. Filter a sufficient quantity through a filter paper (see A, 4) using a funnel heater and then weigh 300 g. ± 1.0 g. of filtered sample into a refining cup. Heat to 105° to 110° C. and then add 3% (9 g.) of A.O.C.S. Official Activated Earth.

7. Stir at 250 r.p.m. for 5 minutes, maintaining the temperature at 105° to 110° C.

8. Filter immediately through a specified paper (see A, 5) using a funnel heater. As soon as the sample filters clearly, collect in a color tube to the 133.35 mm. (5.25 inch) mark and read the color as directed in A.O.C.S. Official Method Cc 13b-45.

TABLES 1 TO 12

TABLE 1: PROPERTIES OF SOME ADSORBENTS DERIVED FROM INDUSTRIAL MINERALS

Adsorbent	Source Material	Activation Method	Activation Temperature °C	Specific Surface m²/gm (2)	Pore Volume cc/100 g	Pore Diam Å	Adsorption Mechanism
Activated alumina	Bauxite	Thermal	300 - 500	50 - 400	40 - 80	70	Physisorption
Bauxite	Natural Mineral	Thermal	250 - 350	80 - 340	30 - 35	50 - 70	Physisorption
Magnesia	Magnesite	Thermal	150 - 200	200			Physisorption
Silica Gel	Silica (via sodium silicate)	Thermal		200 - 800	30 -110	20 - 40	Physisorption
Palygorskite (attapulgite)	Natural Mineral	Thermal	150 - 400	180 - 240	80 - 90	5	
Fuller's Earth	Natural Mineral	Drying	100	80	16 - 22	20	Probably Chemisorption
(Calcium Montmorillonite)	Natural Mineral	Acid	-	100 -300 (3)	85 -105	20	Chemisorption
Sepiolite	Natural Mineral	Thermal	100 - 400	180 -240	-	5	
Bentonite	Natural Mineral	-	-		-	-	Probably Chemisorption
Glauconite	Natural Mineral	Base exchange	-	-	-	-	Ion exchange
Zeolites Natural (1)	Natural Mineral	-	-	200 - 400	18 - 47	2.6 - 7	Physisorption
Zeolites Synthetic	Bauxite, silica etc	Synthesis	100 - 350	400 - 500	47 - 50	4.2 - 7.4	Physisorption

(1) Analcime, chabazite, phillipsite, morderite, erionite, clinoptildite

(2) Nitrogen Adsorption

(3) Intracrystalline channels

TABLE 2: TYPICAL PHYSICAL PROPERTIES OF COMMERCIAL PALYGORSKITE CLAYS

	Colloidal Grade High Volatile Matter	Sorptive Grades Regular Volatile Matter	Sorptive Grades Low Volatile Matter	Sorptive Grades Very Low Volatile Matter
Free Moisture, % loss at 105°C	10 - 17	3 - 17	0	0
Volatile Matter, % loss at 650°C	10	7	2 - 5	1 - 3
Ignition loss % at 1000°C	22 - 25	12 - 16	6 -10	4 - 6
Specific Gravity	2.3 - 2.4	2.3 - 2.5	2.3 - 2.5	2.3 - 2.5
Bulk Density tamped kg/m³	300 - 720	450 - 580	450 - 580	450 - 580
Surface Area BET m²/g	210	125 - 135	125 - 135	125 - 135
Average particle size microns e.s.d.	0.12 - 0.14	Granular	Granular	Granular

TABLE 3: CHARACTERISTICS OF ABSORBENT GRANULES - USA FEDERAL SPECIFICATION P-A-1056A (Absorbent Material, oil & water, for floors & decks)

	Maximum	Minimum
Matter retained on a No. 6 U.S. Standard Sieve	1.0%	0.0%
Matter retained on a No. 30 U.S. Standard Sieve	99.0%	52.0%
Matter retained on a No. 40 U.S. Standard Sieve	99.8%	73.0%
Matter retained on a No. 60 U.S. Standard Sieve	100.0%	90.0%
Ability to absorb lubricating oil (per gm of sample)	-	0.8 mL
Ability to absorb distilled water (per gm of sample)	-	0.9 mL
Solubility in distilled water	1.5%	-

TABLE 4: COMMERCIALLY AVAILABLE PET LITTER PRODUCTS

Product	Absorbency (% of Weight)	Mineralogy
Tydee Tom (old product)	94	Palygorskite
Embassy Absorbent Pet Litter (old product)	113	Illite
Exelcat Litter	80	Calcined Bauxite
Embassy Absorbent Pet Litter (current product)	92	Either Palygorskite or Illite with a calcined product (Mullite and Cristobalite)
Woolworths Absorbent Cat Litter	77	Calcined Bauxite
Kitty Litter	57	Magnesium Oxide

TABLE 5: "TYPICAL" PARTICLE SIZE DISTRIBUTION FOR BLEACHING EARTH USED IN EDIBLE OIL INDUSTRY

Mesh	Microns	Cumulative % Passing
100	150	99
150	104	96
200	76	89
300	53	78
	40	67
	33	56
	27.5	54
	22.5	45
	17.5	34
	12.5	23
	7.5	10
	2.5	2

TABLE 6: SUD CHEMIE - RANGE AND SUITABILITY OF BLEACHING EARTHS

TONSIL OPTIMUM TONSIL OPTIMUM FF	Bleaching earths of highest activity for difficult-to-bleach products such as cottonseed oil, linseed oil, sulphurized olive oil, olive oil, palm oil, fatty acids and fish oils.
TONSIL STANDARD TONSIL STANDARD FF	Preferred qualities for the decolorization of normally bleachable vegetable oils such as soy, peanut oil and rapeseed oil.
TONSIL ACC TONSIL ACC FF	Bleaching earths with lesser activity for easy-to-bleach oils such as peanut oil, sunflower oil, certain mineral oils, as well as for castor oils.
TONSIL L 80 TONSIL L FF 80	High quality special grades for mineral oils, including used oils and oils for metal rolling. Particularly recommended for use at high bleaching temperatures. Because of their special selectivity they are also suggested for certain difficult-to-bleach vegetable oils.
TONSIL L 80 S	Special quality with low moisture content for transformer and similar type oils. This type is free of corrosion producing sulphur, so that silver or copper are not affected.
TONSIL CO GRANULAR (principle particle sizes 15/30, 30/60, 60/90 Mesh)	A granular bleaching earth for the decolorization of mineral oils in the percolation process, for the purification of oils for metal rolling and for the refining of hydrocarbons in vapor phase.
HIGHLY ACTIVE BLEACHING EARTHS TONSIL WITH ACTIVATED CARBON ADDED:	
TONSIL 70 C	For the removal of undesired tints from difficult-to-bleach oils and fats.
TONSIL 60 C	A special product for the removal of undesired tints from certain cotton and sulphurized olive oils.
TONSIL 50 C	A special product particularly for difficult-to-bleach waxes.
TONSIL 35 C	Special grade, recommended for coconut and palm kernel oil.

TABLE 7: AUSTRALIAN PRODUCTION OF BENTONITE & FULLER'S EARTH (1970 - 1976)

Year	Bentonite		Fuller's Earth	
	Tonne	Value ($)	Tonne	Value ($)
1970	352	8 174	-	-
1971	283	8 693	91	906
1972	394	10 000	-	-
1973	899	13 000	30	-
1974	803	18 000	78	1 155
1975	3 350	37 000	18	266
1976	11 954	85 000	9	158

TABLE 8: IMPORTS OF BENTONITE 1970 - 1978

Year	Tonnage		Total Tonnage	Falue f.o.b. A$ ('000)
	U.S.A.	Other Sources		
1970	59 179	7 305	66 484	1 474
1971	87 831	971	88 803	1 887
1972	49 515	346	49 861	1 540
1973	53 902	4 062	57 965	1 390
1974	80 171	5 193	85 363	1 649
1975	49 515	346	49 861	1 540
1976			23 102	708
1977			13 191	558
1978 (Jan - March)			7 215	490

TABLE 9: IMPORTS OF ACTIVATED NATURAL MINERAL PRODUCTS AND ACTIVATED CLAYS

Year	Tonnage	Value ($)
1970	3 868	347 222
1971	2 458	266 106
1972	2 387	247 222
1973	2 250	153 389
1974	2 984	381 332
1975	2 208	214 727
1976	3 385	413 094
1977	3 959	624 000
1978 (Jan - March)	1 043	179 000

TABLE 10: MINERALOGICAL COMPOSITION OF SAMPLES FROM LAKE FROME CONTAINING PALYGORSKITE

Mineral	R696A	R696B	R697	R698	R699	R700
Palygorskite	D	SD	D	D	D	SD
Quartz	A	D	A	A	T	D
Mica/illite	-	A	-	-	-	-
Mixed layer clay	-	-	-	-	-	-
Montmorillonite	-	-	-	-	-	-
Dolomite	-	-	-	-	T	-
Bassanite	-	-	-	A-SD	-	-
Gypsum	-	-	-		-	T
Feldspar	-	-	-	-	-	T
Halite	A	T-A	T	T	A	-
Kaolinite	-	-	-	-	-	-

KEY :	D	Dominant (>30%)
	SD	Subdominant (15-30%)
	A	Accessory (5-15%)
	T	Trace (<5%)
	-	Not detected

TABLE 11: CHEMICAL ANALYSIS OF LAKE FROME SAMPLES CONTAINING PALYGORSKITE

	Weight %					
	R696A	R696B	R697	R698	R699	R700
SiO_2	53.10	68.27	57.68	49.93	45.04	70.48
TiO_2	0.47	0.60	0.52	0.43	0.29	0.59
Al_2O_3	9.05	8.28	9.53	8.01	6.42	8.45
Fe_2O_3	5.83	4.44	6.14	5.14	6.03	4.29
FeO	0.04	0.04	0.04	0.04	<0.02	0.04
MnO	0.04	0.04	0.04	0.04	0.54	0.06
MgO	6.84	2.97	7.10	6.01	8.64	2.93
CaO	0.16	0.08	0.13	4.88	0.82	1.42
Na_2O	4.31	3.24	1.69	1.28	5.99	0.35
K_2O	1.78	2.35	1.98	1.71	0.99	2.15
P_2O_5	0.01	0.02	0.02	0.03	0.02	0.02
H_2O^+	10.76	6.14	9.83	10.83	9.55	5.06
H_2O^-	5.24	2.12	4.62	4.02	7.25	2.73
CO_2	0.10	0.05	0.10	0.30	1.15	0.35
SO_3	0.93	0.76	0.36	7.22	1.72	1.77
Water soluble Cl	4.30	2.90	1.51	1.10	6.44	0.14
Oxygen equivalent for Cl	-0.97	-0.65	-0.34	-0.25	-1.45	-0.03
Total	102.0	101.7	100.9	100.3	99.5	100.8

TABLE 12: SIZE ANALYSIS AND ABSORBANCY

Material	% Retained B.S. 410 Mesh									Water Absorbancy mLs/gm (dry)
	4	6	8	12	16	22	30	44	60	
Tydee Tom (CE 5269)	-	0.3	20.4	61.3	81.4	94.3	98	98.8	99.1	0.62
Embassy (CE 4270)	-	13.7	40.3	62	77.2	88.9	95.6	97.3	98.2	0.80
Embassy (CE 5273)	0.2	29.3	64	86.1	94.3	98.5	99.3	99.6	99.6	0.65
Woolworths (CE 5274)	5.6	26.2	50.7	72.6	85.4	93	96.5	98.5	99.4	0.47
Kitty Litter (CE 5275)	0.1	8.6	24.7	46.3	69.1	88	94.4	97.1	98.5	0.27
Floor-Dry	2.0	13.1	37.1	66.2	89	99.5	99.6	99.8	99.8	0.81
R696A 650°C	13.8	49.9	72.6	90.4	98.5	99.4	99.4	99.7	99.8	0.57
R696B 650°C	17.4	58.8	82.3	93.9	98.7	99.1	99.3	99.5	99.6	0.29
R697 650°C	14.6	58	83	96.9	100					0.53
R698 650°C	10.3	34.9	56	81.5	96.6	98.2	98.9	99.2	99.6	0.46
R699 400°C	27.9	57.8	72	80.9	86.0	89.7	92	94.1	95.7	0.53
R699 500°C	22.6	51.6	67	78.7	85.4	90.7	93.5	96	97.8	0.58
R699 600°C	5.0	38.5	64.7	80.4	89.3	95.8	100			0.62
R699 650°C	20.1	61.8	84.8	96.6	99.3	99.6	99.6	99.6	99.6	0.74
R699 700°C	2.7	23.4	43.9	63.4	78.4	92.7	100			0.55