aqueous HCl and the methyl esters are taken up in petroleum ether, washed free of mineral acid, dried over anhydrous sodium sulfate, filtered, and stripped on a rotary evaporator under reduced pressure at temp not in excess of 60C.

The results obtained for a highly oxidized refined peanut oil proved that all the interfering substances are eliminated by this procedure. This oil, after three successive alumina treatments, still gave HBr titrations equivalent to 1.97% at 3C and 0.35% at 55C calculated as malvalic acid. After conversion to the methyl esters and treatment by the dual column procedure used for crude oils, these values were reduced to 0.00% and 0.01% respectively.

A 9-year-old refined cottonseed oil after petroleum ether-alumina treatment had an HBr equivalent of 1.16% at 3C and the endpoint at 55C could not be determined with precision because of the development of a reddish-brown color, a common occurrence with such oils. The esters formed by methanolysis gave a zero titration at 3C after the dual column treatment and exhibited normal behavior at the 55C endpoint corresponding to 0.42% malvalic acid.

The cyclopropenoid moiety is not affected by the methanolysis procedure. For example, the malvalic acid contents of the refined cottonseed oil samples (No. 8, 12 in Table II) as determined on the methyl esters were 0.42% and 0.63%, respectively; i.e., identical with the results obtained by direct analysis of the oils. Good agreement was also obtained between the analyses of a number of crude cottonseed oils before and after methanolysis (Table IV).

TABLE IV

Analyses of Crude Cottonseed Oils

Type of oil[a]	% Free fatty acid	Iodine value (Wijs)	HBr equivalent at 55C[b] (as % malvalic acid)	
			Oil	Methyl esters
H	1.55	109.0	0.63	......
H	2.16	102.7	0.56	0.57
H	3.89	....	0.59	......
H	4.69	102.3	0.59	0.56
H	4.86	107.0	0.71	0.72
H	5.18	108.9	0.90	0.90
H[c]	0.70	110.6	0.66	0.66
H[c]	0.48	109.8	0.62	......
E	6.49	107.4	0.62	0.60
E	1.14	104.0	0.52	......
MS	3.96	108.0	0.66	......
MS	4.76	103.4	0.60	......

[a] H = hexane extracted; E = expeller; MS = mixed (hexane-acetone-water) solvent extracted.
[b] HBr equivalent at 3C was zero.
[c] Glandless cottonseed.

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Caking Test for Dried Detergents[1]

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Abstract

A test to measure the caking tendency of dried detergents is described. This test has good reproducibility and should be useful in screening new products, studying formulation changes and examing anticaking agents.

The test measures the force necessary to break cylinders formed from test detergents. Forming and breaking forces are extremely critical and are provided by an Instron Universal Tester. The sensitivity of the test demands careful control of the environment; a number of critical factors are discussed. These include test procedure variables such as cylinder length, forming force, forming rate and the time to form the cylinder and product variables such as moisture content and particle size. An increase in the forming force and time, particle size within certain limits and moisture, increase the breaking force.

Results on drum-dried products were found to correlate poorly with spray-dried products. Heavy duty products show a lower caking tendency than do light duty products. Anticaking additives cause a very marked decrease in breaking force.

Introduction

It is often desirable to obtain quantitative comparisons of the caking tendency of different dry detergents, especially in evaluating new surfactants or anticaking additives. Visual observations are often useful but frequently inadequate. Results are qualitative and rather large differences are required for sample difference to be seen.

Previous attempts to measure cakiness have been made. Tests are described in patents claiming additives to decrease cakiness. One test described in a patent (1), claiming the use of aluminum silicate as an anticaking additive, consists of making cylinders of the detergent and measuring its compressive strength along its axis. Our test is based on this line of thinking, but with an improved method for forming the cylinder and for measuring its compressive strength. Other tests described in patents (2,3) consist of placing the detergent in cartons similar to those used in retail trade and exposing them to a humid atmosphere for an extended period of time. The cartons are then carefully opened and the contents poured through a coarse screen. The amount remaining on the screen is considered caked. This test provides a good practical evaluation but does not satisfy the need for early screening.

Our early work indicated that these tests lack control, giving poor reproducibility and sensitivity. Subsequent work led to our current test which offers the following advantages:

1) the reduction of human factors to the very minimum
2) the exact duplication of all mechanical manipulations involved
3) a high precision in reading results

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[1] Presented at the AOCS Meeting, Minneapolis, 1963.

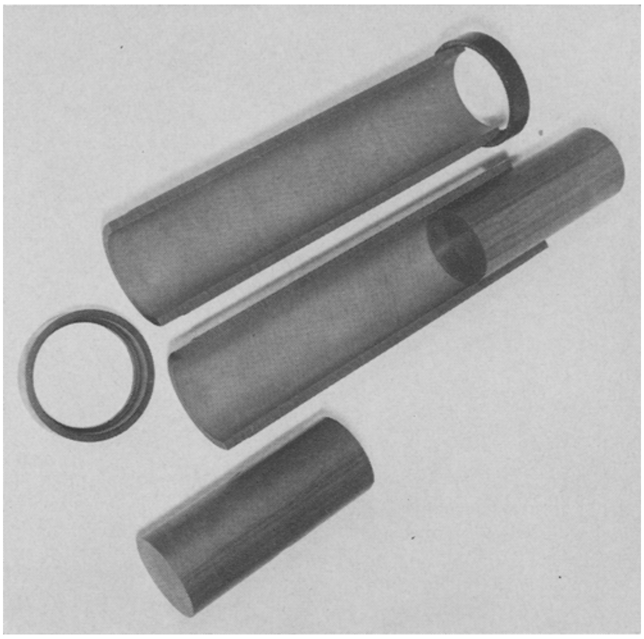

FIG. 1. Mold.

The ability to get quantitative values makes it possible to measure fairly small differences in caking tendency. This makes it possible to show the effect of various product or formulation changes. The good reliability of this test usually makes it possible to compare samples from different test series.

Experimental

The detergent is molded in a hollow cylinder (Fig. 1), inside diam 2 in. and 10 in. long, cut in half along an axial plane. These halves are held together by rings at the ends and the center. Plungers 5 in. in length are fitted to each end of the cylinder. In use, a plunger is fitted to the lower end of the assembled cylinder, the detergent is placed in the mold and the upper plunger put in place. The unit is then placed on an Instron Universal Tester and the force to form the cylinder applied. The detergent cylinder is then removed from the mold and placed back on the Instron for breaking.

The Instron (Fig. 2) is an instrument primarily used for tensile testing of various materials. It is also suited for compressibility testing. Basically, it consists of a moving crosshead supported by two upright screws at each end, which provide the means for moving the crosshead up or down. For compressibility testing such as in this test, the material is compressed between the base and a compression load cell attached to the crosshead. The load cell is connected to a recorder to show the applied force. The rate of movement of the crosshead can be adjusted from 0.02–20 in./min. The speed of the recorder chart can similarly be adjusted. Thus it is possible to apply both the compressing and breaking force at a wide range of speed with a graphic record of all forces involved.

Sample Preparation. Commercial spray-dried household detergents were used in some of our work; however, all of our experimental products were necessarily drum-dried because we don't have a spray dryer suited for experimental work. The drum-dried material is ground to pass through a 14-mesh screen and to be retained on a 200-mesh screen. It is then spread out in large shallow pans and exposed to a constant 50% humidity at 73F for at least 24 hr.

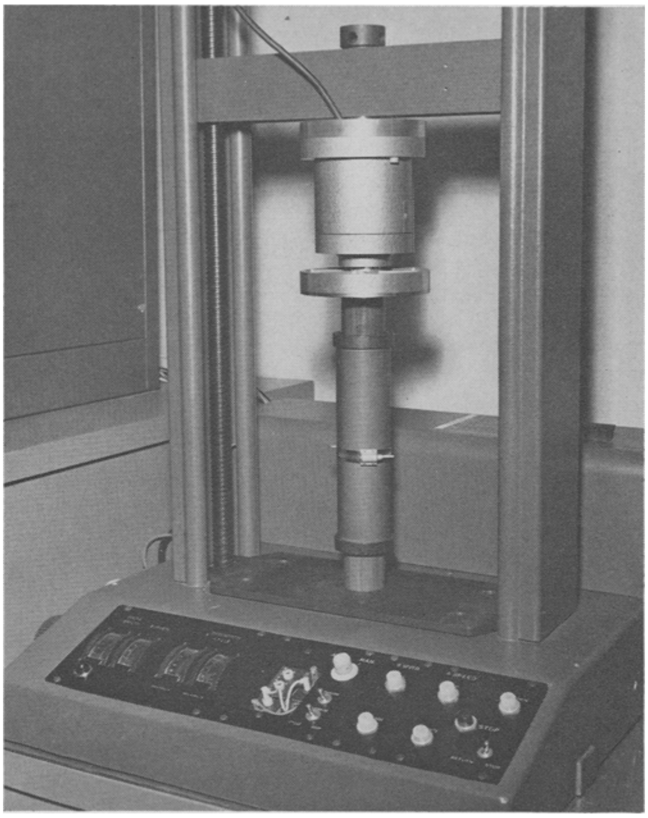

FIG. 2. Instron.

Because screening the product between 14 and 200 mesh does not entirely compensate for thickness variations, it is necessary to control the thickness of the sheet. Because difficulty from sheet thickness is usually caused by a sheet too thick, we discard any part more than about 0.02 in. thick. A sheet too thin also can cause difficulty; however, the formation of too thin sheet is rather rare.

Test Procedure. The procedure developed is as follows: Approximately 200 ml dried detergent is placed in the assembled mold. The volume of the samples should be adjusted to give cylinders 70–75 mm long. The mold containing the sample is placed on the Instron and the compressing force applied at a rate of 0.5 in/min until 80 lb is reached. The crosshead is then stopped and the detergent cylinder still in the mold is allowed to rest for 5 min. The force usually relaxes to ca. 30–40 lb at the end of 5 min, when the Instron's crosshead is backed off and the mold removed. The detergent cylinder is removed from the mold and placed back on the Instron for breaking. The crosshead is lowered at the same 0.5 in./min until the cylinder breaks. Products with a low caking tendency break very sharply; i.e., the breaking force builds up rapidly and then drops off suddenly as the break occurs. Others with a high caking tendency do not break, but rather yield. By yield, we mean the force builds up uniformly to the so-called yield point and as the cylinder yields (bulges out like a barrel) the rate of the force build-up decreases. After the yield point has been reached, the decrease in the rate of the force build-up varies somewhat, depending on the specific product. This yield point is used as the critical value to avoid qualitative measurement problems. Typical breaking curves show in Figure 3. The force required to break or yield the cylinder is the measurement for the test. Higher breaking forces indicate a greater caking tendency.

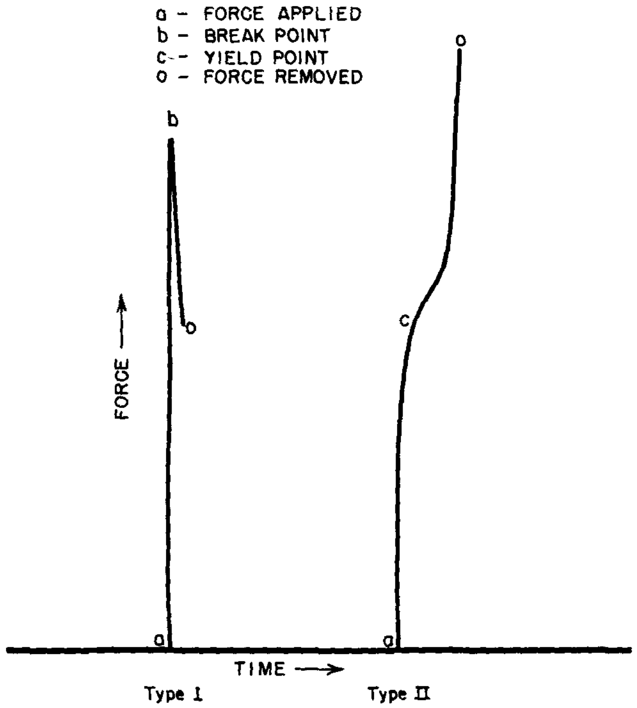

Fig. 3. Typical breaking curves.

Test Variables. The variables examined first were those which might be considered mechanical or test procedure variables. These included such factors as the rate of applying forming force, the maximum force, the time after the maximum force is reached until it is released (this is what we call relaxing time), the rate of applying the breaking force and the cylinder length. Another variable possible with the Instron is the method of applying the forming force. In applying the forming force, it is possible to let the force build up to a predetermined value, then stop the Instron and relax for a period of time. This is the method we chose. It is also possible to maintain a controlled force on the cylinder for any given period.

In the first method the crosshead is brought down at a selected rate until the force on the cylinder reaches a predetermined value, then the crosshead is stopped and held in place. During this period, while the crosshead is held at a constant height, the force on the cylinder decreases, since part of the initial force is the result of friction during compression. In the second method, after the desired force is reached, the crosshead is stopped and when the force decreases to a set value, the crosshead is automatically started up to the original force. Thus the force on the cylinder is maintained within narrow limits as long as desired by the automatic manipulation of the instrument. The height of the cylinder formed by this second method should be less than that of one formed by the first method for comparable average force. It should also be much more tightly packed. It is also probable that product variables would influence the second treatment more than the first.

The second method failed to show any advantages over the first on the basis of a few runs. Consequently, it was not evaluated exhaustively. An auxiliary attachment to the Instron is necessary to maintain the constant force required in the second method. Thus this method would have less general appeal. No objections to the applied force-relaxed technique of

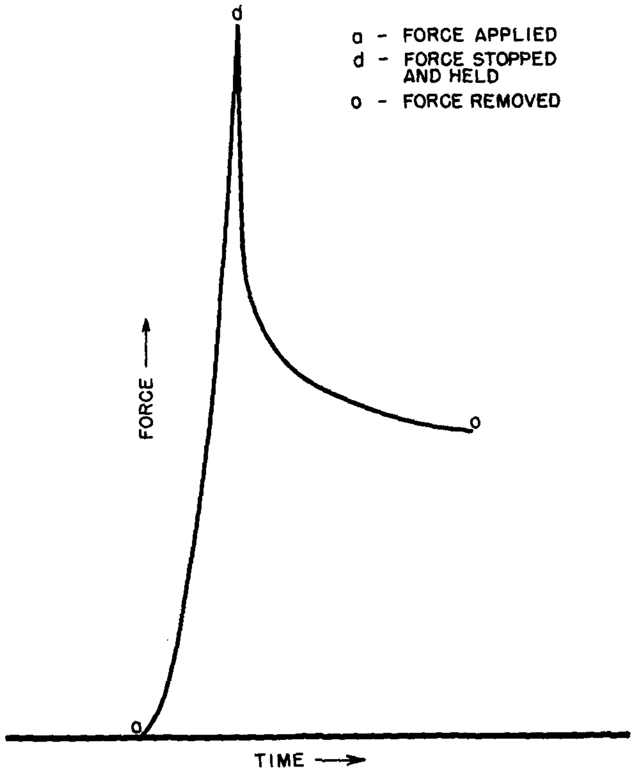

Fig. 4. Typical forming curve.

forming the cylinder were observed. A typical curve showing the forces involved in forming a cylinder by this method shows in Figure 4.

The effects of these test variables on the compressive strength of the detergent cylinder show in Table I. Compressive strength is increased by the following: 1) decreasing the forming speed, 2) increasing the forming force, 3) increasing the relaxing time, and 4) decreasing the cylinder length. Changing breaking speeds from 0.2–1 in./min had no apparent effect on the strength of the cylinder. The rate of relaxing and the force after the relaxing period are factors dependent on the product, rather than these mechanical manipulation.

The cylinder length has a definite effect on the required breaking force. As shown on Table I, the longer the cylinder, the less its strength. This is both a mechanical factor and a function of the product. There is some variation in inherent compressibility or particle configuration which causes some products to compress more or less than others.

Because caking is due to a combination of several factors, which includes compressibility, we should use a given amount of the test detergent and take the measurement on it. However, a more compressible product does not necessarily cake more than a less compressible one in the sense of forming a compact lump, and our interest is in measuring the cohesion of reasonably equal mechanical entities. We adjust the amount of detergent necessary to obtain compressed cylinders which will be from 70–75 mm. The compressibility of a product could easily be measured as a part of the test procedure. However, it might have limited meaning except when prepared under plant conditions.

Product Variables

Moisture Content. If the moisture content of the detergent is too low, the resulting test cylinders are

TABLE I

Effect of Mechanical Variables

Hard to break	Variable	Easy to break
Short	Cylinder length	Long
Slow	Forming rate	Fast
High	Forming force	Low
Long	Relaxing time	Short

generally too fragile to handle; if too high, the cylinders are too plastic to break. Data in Table II shows that relatively small moisture content changes can cause significant changes in the caking test results.

A practical method of controlling this factor is to expose all samples to the same environment. We have available a constant temp and humidity room which is maintained at 50 ± 2% relative humidity and 73 ±2F. All samples are conditioned in this room for at least 24 hr before testing. It is possible that the 50% humidity has a greater effect, good or bad, on some samples than on others. This means that a comparison obtained under this artificial condition could be different from that at ambient atmospheric humidity. However, this risk is really present at any moisture level. Controlling this factor makes comparisons independent of the time of the individual test.

TABLE II

Effect of Moisture Change on Breaking Force

Product	% H_2O	Breaking force, lb
A	11.5	31.1
	10.0	25.2
B	11.0	26.9
	10.0	22.8
C	9.2	28.0
	8.6	17.0

Particle Size. The particle size of the drum-dried test product has a definite effect on the result. In our test the drum-dried material is ground to pass through a 14-mesh screen and to be retained on a 200-mesh screen. Cylinders made from some material run through a No. 5 screen showed considerably more reluctance to breaking than the same material run through a 14-mesh screen, indicating that at least within these limits the smaller particles produce cylinders which are more easily broken.

There is some evidence that the sheet thickness has a significant effect on the results. Variations in sheet thickness cannot be entirely compensated for by the sizing step. This means that drying conditions must be controlled to give reasonably uniform sheet thickness.

Sheet thickness is influenced by several factors. Among the more apparent factors are: 1) the composition of the built slurry, 2) the water content of the slurry, and 3) the type of surface active agent. With some combinations of these factors it is almost impossible to form a sheet. Frequently it is possible to produce an acceptable sheet by increasing the water content or by changing the drum temp or drum speed. If these manipulations are inadequate, then formulation changes may help. Often when working with experimental surfactants, sufficient material may not be available to permit the experimentation necessary to produce a good sheet.

Thick sheets result in large amounts of hard chunks. These chunks cause the formed detergent cylinders to be very fragile, giving low results. Extremely fine sheets, on the other hand, break down into extremely fine particles, which pack together very firmly, and give high results. Difficulty of this nature has been encountered more frequently when working with heavy duty formulations than with light duty formulations. This implies that surfactants with different drying characteristics may not be directly comparable when drum-dried if the drying characteristics cannot be compensated for.

TABLE III

Reproducibility of Results

Product	Average breaking force, lb	
	1st Series	2nd Series
A	31.1	28.5
B	26.9	25.7
C	28.0	31.0
D	20.8	21.8

TABLE IV

Cakiness of Spray-Dried vs. Drum-Dried

Product	Breaking force, lb	
	Spray dried	Drum dried
A	30.1	41.1
B	26.4	35.3
C	29.2	38.2
D	21.3	34.2
E	48.8	74.5

These noticeable effects on caking of particle size with drum-dried products suggest that some variables in spray-dried products could have a similar effect. Because we had no chance to study this effect with spray-dried products, we can only guess at the effects. It is interesting to consider the potential of this test in studying spray-drying variables such as bead size, density and wall thickness on caking.

Reproducibility. In most of our work replicate runs on a sample in one test set usually agree within ±2 lb. When replicate runs do not agree within these limits, the difficulty may be due to a dirty mold which restricts movement of the plunger or unintentional variations in the cylinder length. Other less obvious factors also can be responsible. Reproducibility of several products are illustrated in Table III.

Results

Spray Dried vs. Drum Dried. The study of correlation in caking tendency between equivalent spray-dried and drum-dried detergent is useful because most commercial detergents are spray-dried, while our lab samples were drum-dried. Such a study could allow us to better interpret results obtained with drum-dried products. The simplest way to do this was to run the caking tendency of several commercial spray-dried household detergents and then slurry, drum dry, screen and run the cakiness again. By this treatment we could be sure that the only apparent variable was the physical form.

As we expected, the orders of magnitude of the required breaking force for these two forms were quite different. The rankings were the same, but the degree of differences between samples was not; some differences which were significant between spray-dried products were not significant between their drum-dried form and vice versa.

As can be seen from Table IV, it is difficult to predict the degree of difference between spray-dried

TABLE V

Effect of Additives on Cakiness

	Average breaking force, lb
With 5% toluene sulfonate	30.3
With 5% xylene sulfonate	27.1
Control sample	37.7

TABLE VI

Effect of Active Content on Cakiness

	Breaking force required, lb		
	20% Active	25% Active	30% Active
Drum-dried light duty product....	31.0	37.9	39.8

products from studies on their drum-dried counterparts. It is even more difficult to predict how a product will respond in a heavy duty spray-dried form from studies on light duty drum-dried samples.

Anticaking Agent. It is well known that the addition of certain compounds to dried detergents decreases the caking tendency. Among the more common of these anticaking agents are xylene and toluene sulfonate. This test showed that light duty drum-dried detergents containing 5% xylene or toluene sulfonate have a significantly lower caking tendency. This shows in Table V.

Formulation Effects. The results shown in Table VI indicate the caking tendency of a product varies directly with the active content. This work was done with a drum-dried, light duty formulation.

In addition to changes in cakiness as a results of variation in active content are those brought about by builder changes, i.e., by going to heavy duty formulations. The basic difference is, of course, the replacement of much of the sodium sulfate with polyphosphates. The cakiness of a heavy duty product is generally less than that of a comparable light duty. This does not necessarily mean that any heavy duty has a lower caking tendency than any light duty. The results show in Table VII were obtained using products containing about 30% active sulfonate, and the balance being sodium sulfate and chloride in the light duty with ca. two-thirds of the sulfate replaced with polyphosphate in the heavy duty.

TABLE VII

Light Duty vs. Heavy Duty Formulation

Product	Breaking force, lb	
	HD	LD
Commercial spray dried..............................	7	15
Lab-drum dried..	20.5	35.3

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Some Basic Factors in the Bleaching of Fatty Oils[1]

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Abstract

The physical and chemical properties of bleaching clay are presented, and the effects of these properties upon its performance in bleaching. Various bleaching effects are described:

1) Comparison of atomspheric vs. vacuum bleaching, showing the superiority of one or the other depends upon the predominance of oxidative color fading or color fixation/color formation in the atmospheric bleach.
2) The log-log bleach curve of clays carried out to extreme dosage.
3) Bleaching time-temp effects on different oils, showing that up to a given time, high temp bleaching gives a lighter color than low temp; however, with increased time the high temp bleached oil darkens rapidly in contrast to the low temp oil, which levels out with time.
4) The effect of adding clay to hot oil vs. adding it to "cold" oil, indicating a better bleach when the clay is added to the cold oil, with an explanation for the effect.
5) Comparison of bleaching by filtration of the oil through a layer of clay against conventional bleaching, indicating superiority for the former.

Introduction

VEGETABLE OIL bleaching is a highly controversial subject. Mechanically it is a simple operation: clay is added to oil, followed by increasing the temp to a given level with the oil under agitation, maintaining the temp at that level for a given time, then separating the clay from the oil by filtration. However, the chemical and physical principles underlying bleaching are highly complex and only vaguely understood. In fact the resulting effects on oil color often are so contradictory that bleaching has been termed an "art of witchcraft."

In this presentation an attempt will be made to clarify some of the basic facts about bleaching—specifically: first, to outline the nature of bleaching clay and the theories connected with its use; secondly, to discuss the effects of some of the clay's properties on its performance in bleaching; and last, to describe a number of observed effects in bleaching that appear to follow a consistent pattern.

Nature of Bleaching Clay and Theories of Adsorption

Bleaching clay is produced from a calcium bentonite, which is loosely defined as a clay containing not less than 85% of the mineral montmorillonite (1) on a dry basis. As is well known, there are two types of bleaching clay—natural and activated.

Natural clay is made from bentonite possessing a natural ability to bleach oil, or more correctly, to remove color bodies from oil by the process of adsorption. This bleaching clay is merely dried and milled to a powder with a given particle size distribution.

Activated clay also is produced from calcium bentonite, but it usually is a bentonite that has little ability in the natural state to remove color from oil. In its manufacture the clay is treated with mineral acid, followed by removal of excess acid, before drying and milling.

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[1] Presented at the AOCS Northeast Section Meeting, April, 1963.