

FIG. 4. Oxygen uptake by rat liver homogenates with the following sucrose fatty acid esters: 1, "Sequel 260"; 2, sucrose monostearate B; 3, recrystallized sucrose monostearate B; 4, sucrose monostearate A; 5, sucrose dilinoleate; 6, sucrose trilinoleate; 7, sucrose tetralinoleate; 8, sucrose-safflower oil transesterification product.

various substrates did not correspond to the hydrolytic activity of these substrates with lipase.

The results reported offer little explanation for the intestinal absorption of fatty acid esters without a corresponding increase in serum turbidity on the basis of a hydrolytic mechanism. Thus it will probably be necessary to seek for a physico-chemical or physiological mechanism for this phenomenon.

Summary

Various preparations of sucrose fatty acid esters were hydrolyzed by wheat germ or pancreatic lipase,

pancreatin, pancreatic juice, α -amylase, invertase, or liver homogenates to yield sucrose and free fatty acids as products. The greatest activity was observed with the liver homogenate.

None of the enzymes studied cleaved the glycosidic linkage as indicated by the lack of appearance of reducing groups and by paper chromatography of the products.

The greatest hydrolysis by pancreatic lipase was observed with sucrose esters having a greater preponderance of unsaturated fatty acids, namely, sucrose trilinoleate, sucrose dilinoleate, sucrose tetralinoleate, and "Sequel 260" (69% unsaturated fatty acids).

Sodium taurocholate was required for hydrolysis by pancreatic lipase but not by wheat germ lipase. Sucrose ester was inhibitory to the hydrolysis of triolein by all lipolytic preparations. Tetra-ethyl pyrophosphate and cupric ions were not inhibitory to the hydrolysis of sucrose ester.

Sucrose fatty acid esters supported respiration by rat liver homogenates and to a much lesser extent by rat intestinal mucosa. The rate of oxidation was greater than that observed with sucrose and the corresponding fatty acid. The greatest activity was observed with esters of fatty acids having a greater preponderance of unsaturated fatty acids, namely, "Sequel 260," sucrose di-, tri-, and tetralinoleate.

Acknowledgment

The authors are indebted to Ernest A. Thompson for valuable technical assistance.

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[Received March 1, 1960]

Relationship Between the Apparent Bulk Density of a Bleaching Clay and Its Oil Retention

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OIL RETENTION of bleaching clay is an important economic factor that is often ignored when calculating the comparative cost of clays. The principal reason is difficulty in obtaining an accurate plant oil-retention figure, and thus in many comparative-cost evaluations between two clays the economics

are based upon bleaching power and laid-down clay cost alone. A more complete comparison should include consideration of oil retention as well (2).

The importance of oil retention may be realized by the fact that with oil at 10¢ per pound, every 1% difference in oil retention between two clays, clay-as-

Laboratory Oil Retention Results

Clay	Type	Moisture, %	ABD, lb./cu. ft.	Pot. air space, ^a cu. ft./lb.	% oil retention, clay as charged			
					Test 1	Test 2	Test 3	Average
1.....	Natural	12.0	69.0	.00885	26.3	25.3	25.7	25.8
2.....	Natural	10.2	66.9	.00919	32.6	30.8	29.7	31.0
3.....	Natural	5.3	65.0	.00932	32.6	33.0	32.8
4.....	Activated	16.6	61.8	.01083	34.6	35.1	34.2	34.6
5.....	Activated	18.6	59.0	.01178	42.0	42.8	41.6	42.4
6.....	Activated	19.0	56.0	.01267	46.2	44.7	44.5	45.1
7.....	Activated	12.5	53.2	.01318	52.0	51.2	50.5	51.2
8.....	Activated	14.9	51.3	.01403	52.7	52.4	52.5
9.....	Activated	15.2	49.3	.01484	51.8	51.8	51.2	51.6
10.....	Activated	13.1	49.0	.01484	53.9	53.6	52.7	53.4
11.....	Activated	12.7	42.6	.01787	66.0	65.1	65.6	65.6
12.....	Activated	11.0	39.2	.01981	77.0	78.7	77.7	77.8
13.....	Activated	10.1	38.3	.02035	83.9	82.2	81.0	82.4

^a Equals volume occupied by air voids and water, or

$$\left[\frac{1}{\text{ABD}} - \left[\left(1.0 - \frac{\% \text{H}_2\text{O}}{100} \right) (.00641 [1]) \right] \right]$$

charged basis, is equal to \$2 per ton of clay used. Furthermore activated clays alone vary in oil retention (3, 4) from as low as 27% to as high as 85%.

The writer has observed that an inverse relationship appears to exist between apparent bulk density (ABD expressed as lb. per cu. ft.) and oil retention of clays. This means that the higher the ABD the lower the oil retention, and *vice versa*.

As an illustration, it is generally recognized that Southwestern natural bleaching clays (unactivated) have a lower oil retention than activated clays. The activated clay is leached with mineral acid in its manufacture, which removes a substantial amount of aluminum and other metallic ions from the clay structure. Activated clay therefore is less compact or more "fluffy," contains more air-void space, and thus retains more oil than natural clay after the usual air-and/or steam-blowing of the filter press in the plant.

If the inverse relationship between ABD and oil retention is consistent, the ABD—a simple and reproducible test—might be utilized to estimate oil retention and so eliminate the uncertain and tedious plant procedure for the latter. This article is a study to determine the consistency of the relationship.

Thirteen bleaching clays with ABD varying from 38.3 to 69.0 lb. per cu. ft. were tested for oil retention by the laboratory method below. These data were compared to ABD and oil retention figures reported from seven individual plant tests, each comparing Clays 4 and 6. A considerable amount of clay was used in each test. Sampling of the filter cake was as representative as possible, and its extraction for oil content was conducted with solvents so as to obtain total oil, *i. e.*, the sum of unoxidized and oxidized oil.

Apparent Bulk Density Method

Add clay sample to the 100-ml. mark of a weighed 100-ml. graduated cylinder. Weigh clay and cylinder, and obtain clay weight by difference. Tap the cylinder vigorously on the horizontal surface to constant clay volume. In order to be certain that constant volume is attained, plot ABD after every 50 taps. Use the ABD figure when five of the 50-tap readings in succession show no further decrease in volume.

$$\text{ABD (lb. per cu. ft.)} = \frac{\text{Weight of clay (g.)} \times 62.4}{\text{Tapped volume of clay (ml.)}}$$

Oil Retention Method

Heat 300 g. of refined cottonseed oil with 30 g. of clay sample in the regular A.O.C.S. bleaching equip-

ment, bring the temperature to 248° F. in 5 min., and hold it at that level for 15 min. The latter is necessary to attain a low moisture in the filter cake.

Insert an 11.5-cm. jacketed Buchner funnel into a suction filter flask with a rubber stopper, and keep the steam flowing in and out of the jacket during filtration and subsequent vacuum "blowing." Connect the filter flask to a vacuum pump, and use an 11-cm. filter paper "wetted" with oil prior to filtration.

Filter the slurry of oil and clay by vacuum, then continue to pull the vacuum on the cake for an additional 30 min. In the case of low ABD clays (under 45 lb. per cu. ft.) it is necessary to rotate the flask near the end of filtration in order to avoid cracking of the cake, which otherwise gives an erroneously high retention. It also is advisable to shut off the vacuum when the flask is rotated and resume the vacuum for the 30-minute blowing period after the cake is sucked "dry." This will reduce the amount of suction momentarily.

Scrape all possible filter cake from the filter paper, weigh the cake, and determine moisture on it by heating 5 g. under vacuum at 220° F. for one hour.

$$\% \text{ Oil retention, clay as charged}^a = \frac{[(\text{wt. cake, g.}) (100 - \% \text{H}_2\text{O cake})] - [(30) (100 - \% \text{H}_2\text{O clay})]}{30}$$

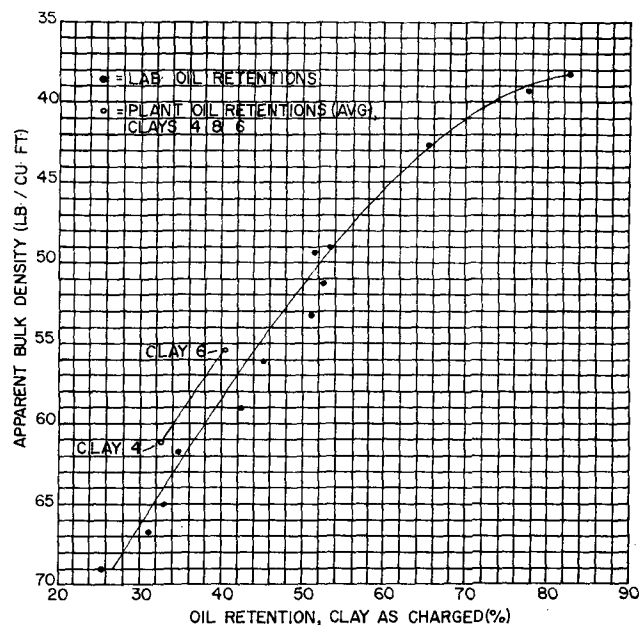


Chart 1. Oil retention *vs.* apparent bulk density.

^a Equals lb. of oil retained by 100 lb. of clay as charged.

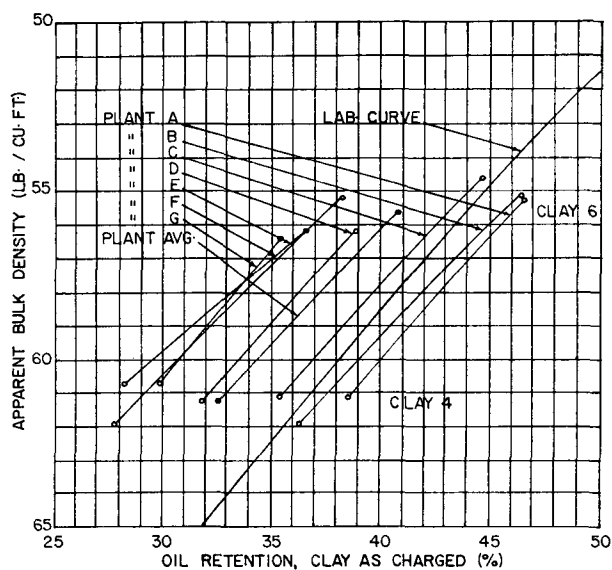


Chart 2. Individual plant oil retentions, Clay 4 vs. Clay 6.

Chart 1 plots oil retention *vs.* ABD for both laboratory results and the average of the seven plant tests involving Clays 4 and 6. Chart 2 plots the individual oil retention *vs.* ABD for the seven plant tests.

It will be observed from Chart 1 that in the case of the laboratory results a reasonably consistent inverse relationship occurred between ABD and oil retention. Also the plant average figures for Clays 4 and 6 paralleled the laboratory curve.

From Chart 2 it will be noted that while the individual plant results on the two clays paralleled the laboratory curve, the oil retentions between plants varied considerably from each other on the same clay. On Clay 4, for example, the retentions varied from 27.8 to 38.4%, on Clay 6 from 35.4 to 46.6%. This is consistent with experience and is the result of different filtration conditions, types of filter-press, and methods of press-blowing between plants.

If the refiner knows that Clay A has a given average oil-retention and ABD over a period of time, he can estimate the oil retention he should obtain with Clay B with a fair degree of accuracy simply by paralleling the laboratory curve in Chart 1 with the ABD of Clay B. Thus, if Clay A has an average oil-retention of 50% and an average ABD of 54 lb. per cu. ft., Clay B with an ABD of 60 lb. per cu. ft. should give an oil retention of 42%.

Summary

Data have been presented which demonstrate that the inverse relationship is reasonably consistent between the apparent bulk density of a bleaching clay and its oil retention.

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[Received November 4, 1959]

Tung Oil Derivatives as Plasticizers for Buna-N Rubber

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NITRILE RUBBER, an oil-resistant acrylonitrile-butadiene copolymer, has been manufactured in the United States since 1939. In order to satisfy the demand by industry today, nitrile rubber is being produced under several different trade names at the rate of hundreds of tons per day. The properties of the vulcanized polymer can be widely varied by changing the ratio of butadiene to acrylonitrile as well as by using different compounding ingredients (1). The type of softener or plasticizer employed often has the ability to impart (to the nitrile rubber stocks) special properties which might be desired by various industries. In general, softeners are used for controlling the hardness and low-temperature flexibility of the materials.

In order to extend the utilization of tung oil and to make available a new source of raw materials, research has been directed toward the development of new chemical derivatives of tung oil suitable as plasticizers or Buna-N rubber softeners. Tung oil is a

triglyceride which contains as glycerides approximately 75% of *alpha*-eleostearic (9,11,13-octadecatrienoic) acid and small percentages of other monoethenoic, dienolic, and saturated fatty acids (2). It has been reported in previous publications from this laboratory that Diels-Alder addition products of certain dienophiles and various esters of the eleostearic acids were satisfactory as primary plasticizers for vinyl chloride-vinyl acetate copolymer (3,4,5,6). Although the adducts of the tung oil itself were not generally compatible as primary plasticizers for polyvinyl chloride, their production is economical because of the limited number of operations required. Since many of these materials contain a number of ester linkages which tend to enhance the compatibility of fatty acids with polar rubbers, such as the nitrile type, it appeared of interest to investigate their suitability as softeners for Buna-N rubber. This paper will describe the preparation and properties of the methyl vinyl ketone, dimethyl maleate, methyl acrylate, and acrylonitrile adducts of tung oil as well as their hydrogenated counterparts and will discuss their plasticizing characteristics for Buna-N rubber.

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