found to be roughly equivalent to the standard deviation of single oven determinations. Certain variables must be compensated for either by method or technique of operation; namely, temperature of sample and density of material in sample tube. The precautions required are determined by the accuracy desired.

The meter has been found to fill a very necessary function in the process control in the milling of oil-bearing materials. The initial cost has been kept at a minimum by designing the meter for specific application, and further the operating and maintenance costs are extremely small. Because of the success we have had with this meter and because experience has shown it to be a valuable process tool, it has been made available to industry for use in whatever application it may be found to serve a useful function.

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Sesamolin Adsorption by Bleaching Agents

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THE Indian oil technologists engaged in the manufacture of Banaspati (edible hydrogenated oil) have to face the problem that certain bleaching earths, although effective in reducing the color of the oil, decompose sesamolin. Most of the bleaching earths produced by manufacturers in sterling areas are of this type, and this has presented a new problem to the industry. A bleaching earth which causes a loss of only a small amount of sesamolin is acceptable, but if it removes the sesamolin completely, either by adsorption or splitting, it should not be used.

With the introduction of the Baudouin test in India as a measure of the sesame oil present in Banaspati, the effect of the bleaching earths and carbons used in processing on the values obtained in the test are of fundamental importance. The characteristic Baudouin test is caused by sesamol ($C_7H_6O_3$), a component of sesamolin ($C_{20}H_{18}O_7$), one of the unsaponifiable components present in sesame oil but not present in other natural oils (1).

Honig (3) showed that acid bleaching earths can lead to the formation of free sesamol. Budowski *et al.* (2) showed that neutral clay and activated carbon, as well as acid clay, can produce free sesamol from sesamolin and can reduce the total of the free and combined sesamol of sesame oil. They also found that nearly all the free sesamol is lost during deodorization of the oil.

This investigation was undertaken to provide additional information concerning the effect of various bleaching clays on the sesamol content of oils for the benefit of manufacturers of hydrogenated oil.

Experimental

1. *William Garrigue Plant.* Twenty-five tons of crude ground-nut oil mixed with 7-10% sesame oil were refined with caustic soda at 60°C. in a steam-jacketed neutralizer equipped with a mechanical agitator. After refining, the oil was settled for 8 hours and siphoned off to a wash tank where it was given several washes with hot water to remove soaps. The amount of sesame oil added to different batches was varied, and the Baudouin tests were conducted on both the crude and refined oils of each batch. The washed oil was bleached in a 12-ton soft bleacher for 1 hour at 90°C. under 27.5 in. vacuum. The effect of different earths in various proportions was noted. The bleached, filtered oil was hardened to a melting point of 37°C. in a 9-ton autoclave. One pound of activated carbon per ton of oil charged was added with the catalyst. The cooled, filtered, hardened oil was given a light alkali wash and several hot water washes. The oil was then treated with different quantities of bleaching earths, and the decrease in Baudouin test color was noted. The bleaching conditions were similar to those used in the soft oil bleacher. The oil was deodorized in a 9-ton deodorizer for 4 hours at 150 to 160°C. under 29.5 in. of vacuum.

TABLE I

Effect of Refining Sesame Oil and Bleaching With 0.5% Clay on Color and Baudouin Test Readings

	Bleaching earth, %	Color	Baudouin test color
1. Crude sesame oil (F.F.A. 2.0%)......	......	4.5Y-0.5R	12.5R-1.0Y
2. Oil after neutralizing..........................	......	....	11.6R-0.9Y
3. Bleached oil a) Fulmond-525 C........	0.5	2.0Y-0.2R	9.5R-0.9Y
4. Bleached oil b) B.C. clay.................	0.5	2.0Y-0.2R	10.6R-0.9Y

2. *Laboratory Experiment.* Sesame oil and different sesame oil mixtures were bleached in the laboratory in 1-lb. batches at 90°C. for 20 minutes, using mechanical agitation and the Baudouin test color noted.

Following the procedure of the Baudouin test, sesame oil is mixed with liquid paraffin as a diluent in the ratio 1:80. Five ml. of this mixture is slightly warmed in a test tube. To this is added 5 ml. concentrated HCl (Sp. Gr. 1.19) and 8 drops of a 2% solution of freshly distilled furfural in neutral alcohol. The test tube is shaken for 2 minutes, and the pink acid layer is allowed to settle for 8 minutes. The acid layer is filtered through a Whatman filter paper, and the filtrate is collected in a 1-cm. cell of a Lovibond Tintometer (British Drughouses Pattern, made in England, Patent No. 299194).

The experimental results obtained are tabulated in Tables I to IV.

In the case of pure sesame oil the dilution in the Baudouin test was 20 times greater than that used for the processed oil.

Discussion of Results

Examination of the data for the plant scale experiment using Fulmond earth in Table III shows that at the end of the processing the sesamoline was virtually completely removed. The data indicate that the Fulmond earth used in the soft oil bleacher split some of the sesamoline into sesamol, which was partially destroyed in the hydrogenator, and the Fulmond earth used in the hard oil bleacher split still more of the sesamoline into sesamol, which was lost during the deodorization. Thus the double bleaching with

TABLE II

Color and Baudouin Test Readings for Groundnut-Sesame Oil Mixture, Using Various Bleaching Agents in the Laboratory Experiments

Nos.	Bleaching agents	Trade	Origin	Color of groundnut-sesame oil mixtures			Baudouin test readings		
				Original	After bleaching with 0.5% agent	After bleaching with 1.0% agent	Original	Oil bleached with 0.5% agent	Oil bleached with 1.0% agent
1	Tonsil	A. C. A.	Germany	2.2Y-0.3R	0.8Y-0.2R	0.6Y-0.1R	1.0Y-13.0R	0.9Y- 9.4R	0.8Y- 6.5R
2	Fuller's earth	311 C	I. C. I.	2.2Y-0.3R	1.0Y-0.2R	0.8Y-0.1R	1.2Y-20.0R	1.2Y-17.0R	1.0Y-15.0R
3	Nuchar (old sample)	....	U. S. A.	2.2Y-0.3R	0.8Y-0.2R	0.6Y-0.1R	0.9Y-11.4R	0.9Y-10.8R	0.9Y-10.0R
4	Fulmond	525 C	I. C. I.	2.2Y-0.3R	0.9Y-0.2R	0.6Y-0.2R	1.2Y-20.0R	0.9Y-16.4R	1.0Y-13.5R
5	Cron (carbon)	"A"	Germany	2.0Y-0.3R	0.7Y-0.2R	0.6Y-0.2R	0.9Y-11.4R	0.9Y-10.2R	0.8Y- 9.3R
6	Texas clay	....	U. S. A.	2.0Y-0.3R	1.1Y-0.2R	0.6Y-0.2R	0.9Y-10.0R	0.9Y- 9.3R	0.8Y- 8.4R
7	B. C. clay	....	U. S. A.	2.0Y-0.3R	1.1Y-0.2R	0.4Y-0.2R	0.9Y-10.0R	0.9Y- 9.5R	0.8Y- 8.4R
8	Darco	97	U. S. A.	2.0Y-0.3R	1.0Y-0.2R	0.6Y-0.1R	0.9Y-10.4R	0.9Y- 9.6R	0.9Y- 9.6R
9	Filtrol	F. O.	Belgium	2.0Y-0.3R	0.9Y-0.2R	0.8Y-0.2R	0.9Y-11.4R	0.9Y- 9.6R	0.8Y- 8.8R
10	Marco (carbon)	....	U. S. A.	2.2Y-0.3R	1.2Y-0.2R	1.0Y-0.2R	0.9Y-10.2R	0.9Y- 9.5R	0.8Y- 8.7R
11	Norit (carbon)	O. L. P.	Germany	2.2Y-0.3R	1.2Y-0.2R	1.0Y-0.2R	0.9Y-10.2R	0.9Y- 9.6R	0.8Y- 8.8R

TABLE III

Baudouin Test Readings at Various Stages of Production of Banaspati, Using Fulmond Earth in Plant Scale Experiments

Processed oil	0.5% of earth 10% sesame oil		0.2% earth 7.0% sesame oil		0.1% earth 7.0% sesame oil	
Crude soft oil	1.3Y-30.0R	1.3Y-30.0R	1.0Y-16.0R	1.0Y-15.0R	1.0Y-15.0R	1.0Y-15.0R
Alkali neutralized soft oil	1.3Y-28.8R	1.3Y-28.8R	1.0Y-15.2R	1.0Y-14.2R	1.0Y-14.2R	1.0Y-14.0R
Bleached soft oil	1.3Y-26.0R	1.3Y-26.5R	1.0Y-14.0R	1.0Y-13.0R	1.0Y-13.2R	1.0Y-13.0R
Hardened oil	1.2Y-20.3R	1.2Y-21.0R	0.9Y-12.0R	0.9Y-10.5R	0.9Y-10.0R	0.9Y- 9.8R
Bleached hard oil	1.0Y-15.0R	1.0Y-14.2R	0.9Y- 9.2R	0.9Y- 8.2R	0.8Y- 8.2R	0.8Y- 8.0R
Deodorized hard oil						
a) 150°C	....	0.7Y- 5.0R	0.7Y- 3.0R	....	....	0.7Y- 3.5R
b) 160°C	0.7Y- 3.6R	....	....	0.7Y- 1.3R	0.7Y- 3.0R	....

TABLE IV

Baudouin Test Readings at Various Stages of Production of Banaspati, Using B. C. Clay in Plant Scale Experiments

Processed oil	0.5% earth 9.0% sesame oil		0.2% earth 9.0% sesame oil		0.1% earth 7.0% sesame oil			
Crude soft oil	1.2Y-24.0R	....	1.2Y-24.0R	....	1.0Y-16.0R	1.0Y-16.0R	1.0Y-15.0R	1.0Y-15.0R
Alkali neutralized soft oil	1.2Y-23.0R	....	1.2Y-23.0R	....	1.0Y-15.2R	1.0Y-15.4R	1.0Y-14.5R	1.0Y-14.6R
Bleached soft oil	1.2Y-21.2R	....	1.2Y-21.8R	....	1.0Y-14.2R	1.0Y-14.5R	1.0Y-13.8R	1.0Y-14.0R
Hardened oil	1.1Y-17.8R	....	1.1Y-18.0R	....	0.9Y-12.0R	1.0Y-12.6R	1.0Y-12.5R	1.0Y-12.2R
Bleached hard oil	1.0Y-15.4R	....	1.0Y-16.8R	....	0.9Y-11.0R	0.9Y-11.6R	0.9Y-11.2R	0.9Y-11.2R
Deodorized hard oil, 150°C	1.0Y-13.0R	....	1.0Y-15.0R	....	0.8Y- 9.5R	0.8Y-10.0R	0.8Y- 9.8R	0.8Y- 9.6R

Fulmond earth left hardly any of the specific material which responds to the Baudouin test in the hard oil. In contrast to this the results obtained with B.C. Clay shown in Table IV indicate very much less loss when this clay is used. Here the drop in Baudouin test is only 11.0 units out of 24.0 when 0.5% clay is used and 5.2 units out of 15.0 when 0.1% clay is used. This indicates a much smaller amount of splitting of the sesamoline in the bleachers by the B.C. clay than by the Fulmond earth.

Experiments carried out on a laboratory scale corroborated the results obtained in the plant scale work. Examination of the data in Table II shows that the decrease in the color of the oil, using 0.5% Fulmond earth, is identical with that when 0.5% B.C. clay is used (1.3Y-0.1R), but the decrease in Baudouin test color was 3.6R for the Fulmond earth and only 0.5R for the B.C. clay. When 1.0% of clay was used, the changes in the color of the oils were again identical, but the Baudouin fall was 6.5R for the Fulmond earth and only 1.6R for the B.C. clay. It may therefore be inferred that the Fulmond earth is equal to B.C. clay in bleaching power, but its destructive effect on sesamolin is 3 or 4 times as great as that of B.C. clay.

This great difference in the two earths with respect to Baudouin fall, which is a vital factor insofar as the usefulness of a clay in the processing of Banaspati in India is concerned, led us to test various other bleaching agents and carbons on a laboratory scale. On the basis of these tests we have divided the bleaching earths and carbons into two groups a) Tonsil A.C.A., Fuller's earth 311 C, Fulmond 525 C, and Filtrol F.O., which are not suitable for use in processing Banaspati, and b) B.C. clay, Texas clay, Cron "A," Nuchar (old sample), Norit O.L.P., Darco 97, and Marco, which are quite suitable.

We find that there is a relationship between the ratio of the decrease in the yellow color of the oil (Y_b) and the Baudouin fall (R_b) for a particular bleaching earth or carbon and its suitability for use in the manufacture of Banaspati. For all the unsuitable earths or carbons $Y_b < R_b$; for all those which are suitable $Y_b =$ or $> R_b$. This relationship is indicated in Figure 1.

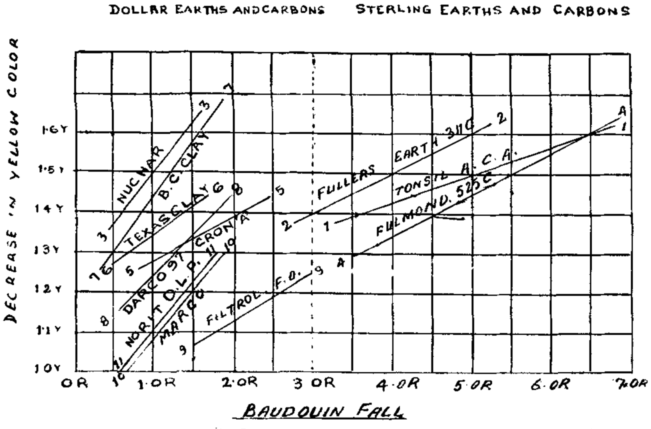

FIG. 1. Relation of decrease in yellow color of oil to Baudouin fall for 0.5% and 1.0% of various bleaching earths and carbons.

This article outlines the relationship of Baudouin fall to bleaching action of various bleaching agents to determine their suitability.

In general, the suitable earths and carbons are manufactured in dollar areas which are inaccessible to Indian importers and manufacturers of Banaspati, and those earths and carbons manufactured in sterling areas, which are open to Indian importers, are unsuitable. This works a hardship on Indian manufacturers of Banaspati as this product is required by law to pass the Baudouin test.

A comprehensive investigation of the effect of different bleaching agents upon the change in color of the oil and of the sesamol and color bodies adsorbed by different earths is now being conducted by the authors.

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Catalysis of Fat Hydrolysis by an Acid Regenerated Cation Exchange Resin

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ION-EXCHANGE resins have been used in recent years as catalysts in a number of chemical reactions. An acid regenerated cation exchange resin (Zeo-Karb H.) was used by Sussman (4) in 1946 as a catalyst for certain esterification and ester hydrolysis reactions. A cation exchange resin (Amberlite I.R. 100) was investigated by Thomas and Davies (5) in 1947 and found to be an effective catalyst for ester hydrolysis. Levesque and Craig (2) have studied the kinetics of esterification by a cation exchange resin, and in a recent paper Schlenk and Holman (3) used an anion exchange resin to catalyze the methanolysis of triglycerides. Hydrolysis of triglycerides, employing an ion exchange resin catalyst, has not yet been reported.

In the Twitchell process of fat splitting a mineral acid is used as catalyst. The use of a cation exchange resin catalyst, instead of a mineral acid, would have many features to recommend it. Corrosion of equipment could be reduced, the resin catalyst could be recovered and used again, and the acid-neutralization stage in the treatment of the crude glycerol-water would not be necessary. Fatty acids produced by fat splitting with mineral acid catalysts are often dark in color, but an ion exchange resin catalyst may yield a lighter product.

It was therefore considered of interest to investigate certain cation exchange resins as fat splitting agents. This paper describes the use of an acid regenerated cation exchange resin (Dowex-50) as a catalyst in the hydrolysis of tallow. The properties and operating characteristics of Dowex-50 have been described by Bauman *et al.* (1).

Materials

The tallow samples used in this investigation were: a) a "special" grade tallow, refined and bleached in the laboratory, b) a "special" grade tallow, used without any further treatment, and c) a No. 1 grade tallow. The catalyst employed was an acid regenerated cation exchange resin (Dowex-50, 200-400 mesh, 12% cross links). The resin was weighed out in the moist condition and used in the hydrogen form. The fat splitting reagent employed was Petronate L (low molecular weight), described by the manufacturer as "a highly refined petroleum sulfonate." This reagent produces a good emulsion of the fat in distilled water and ensures intimate contact of these two components. Reagent grade hydrochloric acid was used for catalyst regeneration.

Experimental Method

In each experiment the reaction mixture consisted of 150 g. of tallow, 60 g. of distilled water, and 2.50 g. of Petronate L. The amount of water used throughout this investigation was maintained at 40% of the weight of tallow. The resin was weighed out in the moist condition. Generally 4.50 grams of Dowex-50 (200-400 mesh) were used as catalyst. This amount was 3% of the weight of tallow.

The weighed amount of resin catalyst was placed in a liter round-bottomed flask. The Petronate L was dissolved in 60 g. warm distilled water, and this solution was poured into the flask. The tallow sample was heated on a steam bath until liquid, and the liquid tallow poured into the flask. The contents of the flask were thoroughly mixed by careful swirling of the flask to produce a fat-water emulsion. This mixture of emulsion and resin catalyst was now refluxed at 100°C. with continuous stirring for 6 hours. Stirring was discontinued after 6 hours, and the emulsion readily separated into two layers. The resin remained at the bottom of the flask in the lower layer of glycerol-water. Fatty acid and glycerol-water layers were separately decanted off from the resin catalyst. The resin particles were washed in the flask with about 500 ml. of distilled water. After the resin particles had settled, the water was decanted off.

The yield of free fatty acids (stated as % oleic acid) at the end of this first stage of the two-stage fat splitting operation was approximately 88%. The resin catalyst was used in the second stage of the fat splitting operation without any further treatment.

In this second stage the glycerol-water was removed and replaced by 60 g. distilled water. The reaction mixture was again refluxed for 6 hours at 100°C. At the end of the reaction fatty acids, glycerol-water, and catalyst were separated. The final yields of free fatty acids (stated as % oleic acid) ranged from 96% to 100% in a number of experimental runs. No additional fat splitting reagent was required for the second stage of the reaction.

A 5 g. sample of fat was removed for analysis for free fatty acids. This fat was dried with Fuller's