The sulfuric index has a place in the record of analysis of cottonseed oil. The conditions entering into this determination can be controlled, but if the results are to have any value the method must be followed with care and expert manipulation. As a routine method it does not compare with that for the iodine number in the number of determinations that can be made in a given time, but as a means of identification of an unadulterated oil it compares favorably. The extent of adulteration of cottonseed oil with olive oil may be determined within a definite limit, but the reverse is not true. A large proportion of cottonseed oil can be added to olive oil, without increasing the index measurably.

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BLEACHING STUDIES ON COTTONSEED OIL

By Frank C. Vilbrandt and Herman J. Bankston, Jr.

The production of a light, clear oil from dark-colored crude cottonseed oil is a difficult industrial undertaking and much time and money has been spent in this study. After the process of dragging down the fine meats and the proteins with soap formed in the oil, which in addition reduces the fatty acid content of the oil, many substances have been suggested for further bleaching the oil, but Fuller's Earth or certain clays are commonly used for this purpose.

There are many grades of this earth as well as many grades of oil to be bleached, some of the latter not responding to this treatment at all. Therefore many investigations have been made to determine whether the variability of the composition or of the procedure is responsible for the variations in results. Some emphasis has been laid upon the effects produced by these earths being dependent upon the quality of the earth, the quality of the oil and the skill of the workman in carrying on the bleaching operations. However, studies carried out by the Bleach Test and Fuller's Earth Committee, A. O. C. S., and embodied in their report[1] of August, 1921, indicated that the time and degree of agitation had no influence of the degree of bleach, that it was unnecessary to fix a standard procedure and the skill of the workman was not such an important matter in the bleaching of the oil.

Chemical analyses seem to throw no definite light on the mechanism of the bleach, for bleaches of the same formula often have different bleaching properties, while others with widely different composition have almost

[1] *Cotton Oil Press*, V, 122 (1921).

identical bleach qualities. Oils are encountered that are not affected by increasing the amount of the Fuller's Earth and the greater the amount of earth used, the greater the introduction of foreign tastes and odors imparted to the oil by the Earth.

Therefore the only practical method of gaging the bleaching power of an oil or the bleaching power of an earth sample is by trying it out, and standardizing against known earth and oil sample.

A review of the different methods of bleaching, suggested to the writers, that there may be some chemical reason for the difference in the bleaches. Holbrook[2] used sodium silicate after the reduction of the free fatty acid content of the oil and the settling out of the soap. This silicate, being alkaline, indicates the probability that the coloring matter is acidic and is neutralized by the sodium silicate or precipitated in this alkaline medium. On the other hand, Baskerville[3] uses a patented inorganic acid solvent that he claims has the properties of Fuller's Earth. The use of sulfuric acid is also known, it being supposed that the acid chars or dehydrates the coloring matter and causes it to become insoluble. Many active bleaching Fuller's Earth samples exhibit the property of giving an acid reaction to water in which they are suspended with phenolphthalein as indicator.

This investigation was undertaken with the purpose of finding out whether the acidity or alkalinity of the solutions or the Earth affected the bleaching property.

Bleaching Agents.—The substances that were used for bleaches on the treated oil were animal charcoal, bone black, Georgia clay, China clay, kaolin, Fuller's Earth, Portland cement and coal clinker. The animal charcoal and bone black were ordinary laboratory stock materials; the Georgia clay was taken from the hillside of the campus of Emory University, Emory, Georgia. The China clay and kaolin were also common chemical stockroom material. The Fuller's Earths used were specially purchased products. The Portland cement used was a common brand of construction material, while the coal clinker was taken from a power plant. Only the clinker was given any mechanical treatment previous to its use; in this case the clinker was ground to pass an 80 mesh screen.

Oil Stock.—Five gallons of fresh raw cottonseed oil was obtained from a press that was operating on fresh, new seeds of the season, the fresh oil being of not a bad color with a small amount of the mucilaginous, fine, mealy matter and some tarry substance. The oil had a fatty acid value of 1.8% and a saponification value of 198 (Hanus Iodine Method).

Since all the samples were to be run for relative bleaching activity, a large portion of the raw oil was treated with caustic and clarified, this clarified and washed sample being used as the standard oil to which all

[2] *J. S. C. I.*, XXXV, 317 (1916).

[3] *J. S. C. I.*, XXXIII, 930 (1914).

the different bleaches were added. The factor of variability in the caustic treatment was thereby eliminated from this study, or reduced to the minimum. The weighed oil was heated to 30°C. and a quantity of caustic soda solution slightly in excess of the amount required to take care of the free fatty acids was stirred in as rapidly as possible, and the stirring continued for ten minutes with an electric agitator, during which time the temperature of the mass was slowly raised to 52°C. The agitation was continued until flocculing occurred and after settling for five hours the clear, but colored, oil was separated from the settlings. This oil was then washed free from caustic alkali with water, maintaining a temperature of 40°C. throughout. After standing several hours the clearer oil was poured off from the watery emulsion and treated with Plaster of Paris to take out the last of the water. The resultant oil constituted the raw material for the bleaching experiments carried out in this study.

Color Comparison.—The suggested practice of color standard oils for bleaching qualities, that of using a specific English Fuller's Earth was not followed. In its place was substituted the easily reproducible chemical color comparator. This color comparator consisted of 400cc. Pyrex beakers of uniform dimensions, placed on an opaque, white glass, and the reproducible K_2CrO_4 color solutions of the following compositions placed therein:

1% K_2CrO_4 solution, neutral, constituted color A, 5% B, 10% C, 15% D, 20% E, 1% K_2CrO_4, with 5 drops conc. HCl per 250 cc. solution color F, and 5% K_2CrO_4, with 10 drops conc. HCl per 250 cc. G.

All color comparisons were made in the same size beakers, at the same time, and using the same volume of oils and color standards.

Bleaching Results.—The general procedure for bleaching was carried out as follows: Three hundred cubic centimeter portions of the oil stock were heated to 50°C. and at this temperature a definite weight of the bleaching material was added and the mixture agitated 20 minutes. The mass was then filtered through filter cloth on a Buchner funnel. The original unbleached, causticized and washed stock gave a color G, which was slightly darker than the crude oil. A sample of salad oil obtained on the market had a color between B and C, while a marketed cooking oil, summer stock, had a color B.

A preliminary run was made to determine the minimum amount of clay that could be used with the above oil and the above treatment to give the best color. Runs using 2%, 3%, 5% and 10% of Fuller's Earth were made. Results with the use of 5% and 10% were the same, color E; 3% gave color between E and F. Therefore the standard quantity of bleach used to reduce the quantity factor to the minimum in this study was adopted as 5%.

Table 1 sums up the results, giving also the conditions under which the bleaching materials were treated before use.

TABLE 1

BLEACHING PROPERTIES OF COMMON OIL BLEACHES

Experiment No.	Bleaching agent	Condition of bleach	Color comparison results	Troubles in filtering
A	ORIGINAL CRUDE OIL	Raw, none	F-G	
B	Raw treated oil stock		G	
1	Fuller's Earth, No. 1	Raw, untreated	F	None
2	Fuller's Earth, No. 1	Heat 1 hour at 105°C.	E	None
3	Fuller's Earth, No. 1	Heated 1 hr. over Meker burner	D	None
4	Fuller's Earth, No. 1	Wetted, then dried at 105°C.	D	None
5	Fuller's Earth, No. 2	Raw, untreated	F	None
6	Fuller's Earth, No. 2	One hr. drying at 105°C.	E	None
7	Kaolin	Raw, untreated	G	Slight (small cloudiness remained)
8	Kaolin	Heated 1 hr. over Meker burner	C	Slight, (slight cloudiness remained)
9	China Clay	Raw, untreated	G	Difficult to filter
10	China Clay	Heated 1 hr. over Meker burner	F	Difficult to filter
11	Animal Charcoal	Raw, untreated	GG	Could not filter out the char
12	Animal Charcoal	Heat 1 hr. over burner	GG	Could not filter out the char
13	Boneblack	Raw, untreated	GG	Could not filter out the char
14	Boneblack	Heated 1 hr. over burner	GG	Could not filter out the char
15	Clinker	Ground original clinker	GG	Could not filter out the char
16	Clinker	Heated 1 hr. over Meker burner	GG	Could not filter out the char
17	Portland Cement	Raw, stock	G	None
18	Portland Cement	Heated 1 hr. over Meker burner	G	None
19	Georgia Clay	Air dried	E	None
20	Georgia Clay	Dried one hour at 105°C.	F	None
21	Georgia Clay	Heated 1 hr. over Meker burner	B	None
22	Georgia Clay	Same as 21 only used 3% of clay	C	None
23	Georgia Clay	Saturated with concn. HCl, washed 6 times, then dried at 105°C.	G	None
24	Georgia Clay	Saturated with 10% HCl, washed 6 times, then dried at 105°C.	D	None

Experiment No.	Bleaching agent	Condition of bleach	Color comparison results	Troubles in filtering
25	Georgia Clay	Saturated with 10% HCl, washed 6 times, then heated over Meker burner	C	None
26	Georgia Clay	Saturated with 10% NaOH, washed 6 times, then dried at 105°C.	G	None
27	Georgia Clay	Saturated with 10% NaOH, washed 6 times, then heated 1 hr. over Meker burner	F	None

DISCUSSION: It is seen that the clinker, China clay, kaolin, cement, bone black and animal charcoal are unsuitable under the conditions described above because of the difficulty in separating the bleach from the oil. Of these substances only China clay and kaolin after heat treatment have any bleaching properties. The bleaching results one expects with bonechar and charcoal were not present or at least not apparent, due to the large amount of unfilterable char that remained in the oil. The time allowed to permit the suspended solids to settle was varied, but no decolorization was apparent after settling.

Fuller's Earth on heating "boiled" violently, due to the liberation of gases, but in the bleaching tests the results indicating that these gases were not necessary for the bleaching quality of the earth. The fact that the wetted sample of Fuller's Earth, later dried, gave better results than the raw, indicates that if the gases absorbed were CO_2, the water assisted in eliminating them by dissolving some and being driven off on heating, that CO_2 is not an assist to the bleaching properties of Fuller's Earth.

Studies of effect of acidity or alkalinity were made on the Georgia clay, because the preliminary study showed that no odor was left in the oil when this clay was used, while the oil treated with Fuller's Earth retained a distinct odor, or rather an odor was imparted to it. It is evident that the less the hydrochloric acid treatment, the better the grade of product, but that the same relationship holds true about causticity. It is apparent that the hydrogen-ion concentration of the bleach substance and the oil must be well regulated within certain limits and the bleach may be slightly acid.

The following conclusions are based upon the assumptions that holding the oil sample constant and the quantity of bleaching substance at 5% by weight, (*a*) that there is a better bleaching action with a slight acidity than with slight basicity, but that stronger acidity or basicity decreases this property; (*b*) that the Georgia clay used imparted less odor to the oil than the Fuller's Earth used; (*c*) that revivification of nearly all bleaches increase their bleaching power; (*d*) that the phenomenon seems to be a capillarity absorption one.

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