Improved Process for Re-refining Cottonseed Oil for the Removal of Color Bodies[1]

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REFINING records of the Producers Cotton Oil Company for several years have shown that satisfactory reduction in color during refining of some types of crude cottonseed oil is becoming increasingly difficult. Similar observations have been made by others with respect to oils from the High Plains area of Texas, the Rio Grande Valley, and, in some seasons, in the Southeastern and Mississippi Valley areas.

It is a matter of practical observation, confirmed by extensive experimental investigations[2] at the Southern Regional Research Laboratory at New Orleans for nearly 10 years, that the color of crude cottonseed oil is affected to various degrees by the following factors: a) climatic conditions under which the seed is produced and harvested, b) soil conditions and fertility, c) length of time and method of storage of seed, d) milling conditions, especially moisture, temperature of cooking and tempering, time, and pressure of pressing, and e) temperature at which the oil is stored.

The color quality of the refined oil produced from highly colored, crude cottonseed oil may be lowered by improper handling in the refinery. Some oil mills can make a relatively good grade of crude oil even from damaged seed, or at least an oil which can be handled satisfactorily in the refinery.

It is a matter of experience that the quality of a refined oil is more closely related to the quality of the crude from which it was produced than it is to the seed from which the crude oil was produced. For example, for three consecutive seasons the refinery at Fresno has received crude oils from two different out-of-state oil mills located less than 50 miles apart. The seed was from one variety of cotton grown on the same type of soil and under the same climatic conditions. One of the mills produced a crude oil which had a very low refining loss and low refined oil color, but the bleach color exceeded that for Bleachable Prime Summer Yellow grade. The crude oil from the other mill was similar to that produced by the first mill, except that it had a very low bleach color. Obviously the oil from the first oil mill had been damaged in some way during processing.

Regardless of the cause of the impaired color of the crude oil, it is the refiner's responsibility to produce a good quality of refined oil with as low refining loss as possible.

It is generally more difficult to remove residual color from soda-neutralized and degummed oil or to re-refine dark colored refined oils than it is to remove color bodies in the initial refining of the corresponding crude oils. In refining crude oil containing appreciable percentages of free fatty acids the caustic soda appears to disperse rapidly and uniformly, and the soapstock produced in neutralizing the free acidity serves to absorb the coagulated color bodies. However in refining soda ash-neutralized and degummed oils or in re-refining dark colored refined oils containing little free fatty acid, dispersion of the caustic soda does not occur readily in the oil phase, and the amount of soapstock formed is too small to effect efficient absorption of the residual color bodies. It should follow therefore that if the caustic soda could be more uniformly and rapidly dispersed in the oil phase than is the case in accepted refinery practice, better color removal should be obtained. Methods of obtaining improved dispersion of the caustic soda in the oil include higher speeds of agitation than are commonly employed, and the application of high rates of shear or chopping of the aqueous and oil phases.

In December of 1949 experiments intended to test this hypothesis were undertaken. The first experiments were made with a Waring Blendor, and it soon became apparent that the removal of pigments from cottonseed oil in the presence of aqueous caustic soda was a function of a number of seemingly independent variables, namely, a) speed of agitation, b) contact time of oil and alkali during agitation, c) percentage by weight of caustic soda solution used, d) concentration of the caustic soda solution, e) initial temperatures of oil-alkali dispersion, and f) shearing effect of the agitator.

Experimental

To investigate the effect of speed of agitation and shear on color removal, experiments were carried out with the Waring Blendor (10,000 r.p.m.), a Brookfield laboratory mixer (3,000 r.p.m.), and a two-stage Manton-Gaulin laboratory homogenizer. All of the oils used were expeller-pressed and soda ash-neutralized and degummed.

The laboratory investigations were made parallel with pilot plant work and subsequently were applied in full scale plant operation. Some of the basic observations and experimental work are reported here.

The data in Table I illustrate the effect on the bleach color of alkali concentration and time of agitation at 3,000 r.p.m. (Brookfield mixer) with three different soda ash-neutralized and degummed cot-

TABLE I

Effect on Bleach Color of Concentration of Sodium Hydroxide and Time of Agitation at 3,000 r.p.m. on Re-refining Cottonseed Oil

Conc. of NaOH ° Bé	Time of agitation,[a] min.	Cottonseed oil[b]			
		A	B	C	D
20	0	....[c]	....[c]	....[c]	....[c]
	1	4.1	4.5	4.4	6.2
	2.5	4.0	4.0	4.1	5.3
	5	4.0	3.6	4.0	3.9
	7.5	3.8	3.6	3.8	3.6
	10	3.8	3.6	3.6	3.4
30	1	2.6	2.0	2.2	3.2
	2.5	2.4	1.9	2.1	2.9
	5	2.2	1.8	2.0	2.6
	7.5	2.1	1.7	1.9	2.4
	10	2.0	1.6	1.8	2.4
40	1	1.8	1.3	1.7	2.1
	2.5	1.7	1.2	1.5	2.0
	5	1.7	1.1	1.3	1.8
	7.5	1.5	0.9	1.2	1.7
	10	1.5	0.9	1.0	1.6

[a] Brookfield mixer.
[b] Expeller-pressed, soda ash-neutralized and degummed.
[c] Too dark to read.

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[1] Presented at the 24th Fall Meeting of the American Oil Chemists' Society, San Francisco, Calif., Sept. 25-29, 1950.

[2] Reports of many of these investigations have appeared in this Journal.

tonseed oils identified as A to C. In each case the temperature of the oil at the start of the refining was 80°F. The weight of solid sodium hydroxide contained in the 20, 30, and 40° Bé caustic soda solutions in Table I was the same. Only the weight of water used in making up these solutions was different. In other words, for each 500-gram sample of oil, 20.5 grams of 20° Bé caustic soda, or 12.5 grams of 30° Bé caustic soda, or 8.4 grams of 40° Bé caustic soda, was used. The different weights of the different alkali solutions contained the same amount of solid sodium hydroxide.

It is apparent from the data in Table I that the length of time that the oil and caustic soda solution was stirred had an effect on the removal of color bodies. The concentration of the sodium hydroxide solution however had a far greater effect than had the length of time of agitation. Under optimum conditions the removal of pigments proceeds most rapidly during the first five minutes and in many cases is largely completed after two minutes of agitation at 3,000 r.p.m.

In order to determine the effect of speed of agitation on the reduction of the bleach color of a soda ash-neutralized and degummed oil, parallel experiments were made at 3,000 r.p.m. (Brookfield mixer) and at 10,000 r.p.m. (Waring Blendor) with the results shown in Table II. The two agitating devices differ in both rotational speed and type of mixing. Reference to Table II indicates that the greater the rotational speed of agitation, the greater the color reduction, especially with the weaker solutions of caustic soda. For a given time of agitation the Waring Blendor, with a speed of 3⅓ times greater than the Brookfield mixer, removed about as much color from the oil when 30° Bé caustic soda was used as the latter mixer removed when 40° Bé caustic soda was used. When the data in Table II were plotted graphically, it was observed that in the case of 30° Bé caustic soda the curves for agitation at 3,000 and 10,000 r.p.m. were separated by about 1.0 Lovibond red unit while in the case of 40° caustic soda the two curves were separated by only about 0.6 Lovibond red unit.

TABLE II

Effect on Bleach Color of Time of Agitation During Re-refining Cottonseed Oil D

Conc. of NaOH °Bé	Time of agitation, min.	Bleach color, Lovibond red units when refined at	
		3,000 r.p.m.	10,000 r.p.m.
20	0	....[a]	....[a]
	1	6.2	4.2
	2.5	5.3	3.8
	5	3.9	3.4
	7.5	3.6	3.1
	10	3.4	3.0
30	1	3.2	2.2
	2.5	2.9	1.8
	5	2.6	1.8
	7 5	2.4	1.7
	10	2.4	1.4
40	1	2.1	1.5
	2.5	2.0	1.4
	5	1.8	1.2
	7.5	1.7	1.0
	10	1.6	1.0

[a] Too dark to read.

The relation between bleach color and the amount of caustic soda (in percentage) added to a given amount of oil is illustrated by the data in Table III. In the case of the 20° Bé caustic soda no further color removal was obtained with cottonseed oil D at a speed of 3,000 r.p.m. (Brookfield mixer) after 2.5% caustic soda was added. In the case of the 30° and 40° Bé caustic soda a slight improvement in color removal was obtained as the amount of added caustic soda was increased. However the refining loss increased rapidly as a result of saponification when the amount of alkali added was increased, especially with the higher concentrations of sodium hydroxide solutions.

TABLE III

Effect on Bleach Color of the Amount of Sodium Hydroxide Used in Re-refining[a] Cottonseed Oil D

Amount of NaOH used, %	Bleach color, Lovibond red units		
	20° Bé NaOH	30° Bé NaOH	40° Bé NaOH
0	....[b]	....[b]	....[b]
1.5	5.1	3.1	2.1
2.0	4.9	2.8	1.7
2.5	4.5	2.6	1.5
3.0	4.5	2.5	1.4
3.5	4.5	2.3	1.3
4.0	4.5	2.2	1.2

[a] Speed 3,000 r.p.m. (Brookfield mixer), 5 minutes of agitation.
[b] Too dark to read.

The refining loss increased only slightly at low temperatures but increased rapidly at higher temperatures as the time of agitation was prolonged.

In order to eliminate the effect of differences in the type of agitation a series of experiments were made with the Brookfield mixer in which the speed was varied between 800 and 6,000 r.p.m. for a constant time (5 minutes) of stirring, starting with the oil in each case at 80°F. The results are shown in Table IV. Irrespective of the concentration of caustic soda used, the reduction in color increased with increasing speed up to about 4,000 r.p.m. Between 4,000 and 6,000 r.p.m. there was very little improvement in the bleach color of the oil, and in some cases it actually decreased. The latter behavior was found to result from the increase in temperature arising from the frictional heat generated at high stirring speeds.

The effect of temperature of re-refining on the bleach color was verified as follows:

> Using a constant speed of mixing (3,000 r.p.m., Brookfield mixer) and a constant time of 5 minutes, the temperature of the oil at the start of each experiment was increased in increments of 10°F. from 60° to 110°F. A plot of the bleach color *vs.* temperature for each concentration of caustic soda showed that maximum color removal for cottonseed oil D occurred between 70° and 80°F. Less reduction of color occurred in every case when the temperature increased above 80°F. It was also found that the temperature increased from 80° to 102°F. after stirring for 5 minutes at 6,000 r.p.m. with Brookfield mixer, which observation accounts for the poorer removal of pigment bodies occurring at this speed.

Mixing can be obtained by means other than stirring, for example, by forcing a liquid stream through a homogenization valve. In order to compare the effectiveness of this type of agitation with mechanical stirring, a number of experiments were carried out with a Manton-Gaulin homogenizer. In this equipment mixing is accomplished through the action of a valve, the seating faces of which are quite wide and are carefully ground and lapped so that a perfect seal is assured. Pressure is applied to this valve until, at 16,000 p.s.i.g., the opening between the valve faces is approximately 0.003 of an inch. A piston forces the liquid through the valve at the rate of 28,000 to 30,000 feed per minute. Subsequent to passing through the valve, the liquid strikes the valve housing. The combination of high velocity through the valve and shattering against the valve housing produces the shearing effect.

Two variables, concentration of caustic soda and pressure, were investigated. It was found that comparatively low pressures were required to reduce the bleach color of the cottonseed oils used. There was little further improvement in color removal with increased pressures, i.e., above 1,000 and up to 3,000 p.s.i.g. The use of a two-stage system of homogenization was no more effective than a one-stage system. The initial pass through the homogenizer requiring a fraction of a second, reduced the bleach color of cottonseed oil as well as any elaborate recycling system.

With cottonseed oil D, the color removal was approximately the same in a fraction of a second as it was after stirring for 5 minutes at 3,000 r.p.m. (Brookfield mixer) when the same amounts of 30° caustic soda were used. With 40° caustic soda the homogenizer produced approximately the same reduction in color in a fraction of a second as occurred with stirring at 10,000 r.p.m. (Waring Blendor) in 5 minutes.

TABLE IV

Effect on Bleach Color of Varying the Speed of Agitation on Re-refining Cottonseed Oil D

Speed of agitation,[a] r.p.m.	Bleach color, Lovibond red units, after refining with caustic soda		
	20° Bé NaOH	30° Bé NaOH	40° Bé NaOH
0	....[b]	....[b]	....[b]
800	5.1	3.6	3.6
1600	5.1	3.3	2.5
3200	4.1	2.6	1.9
4000	4.0	2.2	1.9
5000	3.9	2.4	1.6
6000	4.0	2.2	1.6

[a] Brookfield mixer.
[b] Too dark to read.

Discussion

All of the work reported above was carried out with expeller-pressed, soda ash-neutralized, and degummed cottonseed oils. In general, the oils were too dark after bleaching by the official method of the American Oil Chemists' Society to be matched with Lovibond red and yellow glasses. When re-refined by the official A.O.C.S. method and then bleached, the color was darker than when the same oils were re-refined with high speed agitation followed by bleaching by the A.O.C.S. method.

It was found that several factors affected the final bleach color. Each of the factors was varied independently until, for all practical purposes, it attained a constant value. The factors included speed of agitation, time of agiation, concentration of caustic soda, and temperature.

It was found that re-refining with agitation below a certain critical speed has very little effect in removing the color bodies of soda ash-neutralized cottonseed oils. For readily decolorized oils, an agitator speed of 1,800 r.p.m. is adequate. With dark colored oils agitation at 3,600 r.p.m. is more efficient. With very dark-colored oils agitation at both 1,800 and 3,600 r.p.m. may be necessary to produce an acceptable bleachable oil. There is also an upper critical limit to the speed of the agitation beyond which effective removal of color bodies ceases. The upper limit results from an increase in temperature caused by the frictional heat of stirring.

Agitation for about 5 minutes produces nearly maximum removal of color bodies although a small additional amount of color is removed if the agitation is continued for an additional 5 minutes.

The percentage by weight of caustic soda also has critical range of effective color removal. Relatively large percentages of 20° Bé or weaker caustic soda solution can be used at temperatures below 85°F. without encountering unduly large refining losses. With higher concentrations of caustic soda solution it is essential to use the minimum percentage by weight of alkali in order to avoid unduly high refining losses.

The temperature of the oil-caustic soda mixture is likewise critical. The removal of color bodies is more complete at temperatures below 80°F. The refining loss increases with increased temperature above that where optimum color removal occurs. Temperature control is especially important when caustic soda solutions more concentrated than 20° Bé are used.

The laboratory observations reported and discussed above have been applied practically in the refinery for processing an average of 3½ tank cars of expeller-pressed, soda ash-neutralized, and degummed cottonseed oils per day. For flexibility of operation, re-refining kettles are equipped with direct motor driven stirrers operating at 1,800 and 3,600 r.p.m. Sometimes it is necessary to refine at both speeds to attain the maximum removal of color bodies.

It was found in the refinery as in the laboratory that the efficiency of color removal is directly proportional to the strength of the caustic soda solution used, the length of time of high speed stirring, the percentage of caustic soda used, and the speed of agitation, and is inversely proportional to the temperature of the oil-caustic soda mixture.

In general, it has been found preferable to use strong caustic soda solutions under the following conditions: a) low percentage by weight of caustic soda solution, b) temperature of the oil-caustic soda mixture below 85°F., and c) addition of water to the emulsion formed by high speed mixing before breaking it with heat.

Similar reduction in color can be obtained with at least one type of homogenizer, but the high initial investment and the power consumption of the homogenizer make it less attractive for re-refining cottonseed oil in large-scale operation than the less expensive stirrers.

Summary

A method for removing color from neutralized and degummed cottonseed oil is described. Data included shows color removal to be directly correlated to: a) concentration of sodium hydroxide solution, b) length of time of agitation, and c) speed of agitation in r.p.m. The degree of color removal is inversely correlated to the temperature of the oil during agitation with sodium hydroxide solutions. Laboratory find-

ings have been put to practical use in the refinery for over a year with satisfactory results.

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Report of the Seed and Meal Analysis Committee, 1950-1951

THE work of the committee is currently conducted by five subcommittees. Status and report of them are as follows:

The Subcommittee on the Analysis of Flaxseed and Linseed Meal has written up methods for sampling, moisture, oil content, protein, and ash in flaxseed, and methods for sampling, moisture, oil content, protein, ash, and crude fiber in linseed meal. These methods are now undergoing collaborative checking. The results of analytical testing have been encouraging, and it appears probable that the methods will require only minor editorial revision before submitting for approval to the Seed and Meal Analysis Committee.

The Subcommittee for the Analysis of Copra and Copra Meal has carried on some correspondence relative to its assignment. It met and discussed the problems at the time of the fall meeting of the Society. It was agreed that the subject of determination of moisture and volatile matter should be considered first. Plans were made for exchange of analytical methods, prior to carrying out collaborative work. It is anticipated that the first collaborative work will be started soon.

The Subcommittee on the Analysis of Tung Fruit and Meal is continuing its work on methods. A report on its efforts will be offered later as the season of harvest does not permit completion of the year's work at this date.

Report of Subcommittee on Peanut Analysis

Variations in analysis reported on the Smalley Foundation check samples of peanut kernels have led to doubt of uniformity in the mixing of the sliced samples. The requiring of the use of an instrument such as the velocity mixer is indicated. In order to determine the efficiency of the velocity mixer in the preparation of sliced peanuts for analysis, a series of samples were prepared and sent to five laboratories for analysis.

Three samples, A, B, and C, were prepared. Samples A were prepared by slicing several pounds of Southeastern Runner Peanuts and mixing by rolling back and forth on a sheet of paper. Samples A were then taken at random and sealed in 6-oz. salve tins. Samples B were similarly prepared from Virginia peanuts. These samples were so selected in order to obtain as wide a variation as possible in oil content so that inefficiency of mixing would be most pronounced. Samples C were prepared separately by weighing 20 grams each of Samples A and B and mixing for 30 seconds in the velocity mixer. These 20-gram portions were all taken at random from the larger preparations.

Each collaborator was instructed to make triplicate oil determinations on each sample and to mix 20 grams each of Samples A and B and determine oil content in triplicate, moisture to be determined simultaneously with the oil. The composite sample was to be mixed as was customary in each laboratory. All collaborators used the velocity mixer with the exception of No. 4. He reports that mixing was done by hand.

The results of all individual tests are shown in Table I. All results were calculated to a dry basis for purposes of comparison.

TABLE I

Percentage of Oil in Peanut Kernels, Moisture-Free Basis

Collaborator No.	Sample			
	A	B	C	Mixed A & B
1	52.41	44.87	48.11	48.66
	52.41	44.66	48.63	48.56
	52.36	44.71	48.50	48.56
Avg.	52.39	44.75	48.41	48.59
2	53.05	45.92	49.08	49.24
	52.90	45.92	49.24	49.24
	52.90	46.02	49.24	49.09
Avg.	52.95	45.95	49.19	49.19
3	52.59	44.98	48.79	48.76
	52.63	45.05	48.78	48.81
	52.64	45.04	48.82	48.83
Avg.	52.62	45.02	48.80	48.80
4	52.63	45.04	48.94	48.63
	52.59	45.10	48.94	48.52
Avg.	52.61	45.07	48.94	48.58
5	52.62	45.22	48.79	48.74
	52.72	45.16	48.95	48.64
	52.77	45.00	49.00	48.69
Avg.	52.70	45.13	48.91	48.69

It is obvious that if results obtained on Sample C (mixed prior to sending to each collaborator) and the mixed sample (prepared from A and B by each collaborator) are in agreement, the method or methods of mixing are satisfactory. This agreement is shown in Table II, where the high and low results on C and mixed A and B samples are shown for each col-

TABLE II

Highest and Lowest Result Obtained on Either Sample C or Composite of A and B

Collaborator	1	2	3	4	5
High	48.66%	49.24%	48.83%	48.94%	49.00%
Low	48.11%	49.08%	48.76%	48.52%	48.64%
Total Spread	0.55	0.16	0.07	0.42	0.36