Vegetable Oil Refining Procedures

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THE well-known refining methods employing caustic soda and soda ash have been described in the literature, and up to the present these methods have been very efficient. But the methods of expressing vegetable oil from the seed and bean have changed radically the last year or two in that about 75% of all the soybean oil produced is by solvent extraction and a noticeable portion of cottonseed oil is produced by pre-expelling, employing mechanical screw presses and extracting the cake or meal residue with the standard solvent extraction equipment as well as changing from hydraulic to mechanical pressing but retaining the hydraulic cooking method.

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The success that was obtained from extracting soybean oil has offered little difficulty to the refiner. The solvent oil is usually considered superior to the screw press expeller method and far superior to the hydraulic method. On cottonseed oil, largely due to the different coloring matter, solvent extraction has not advanced as far as it has on soybean.

It was learned early in the first attempt to extract cottonseed at Wilson, Ark., that the heat and time employed to remove the solvent from the oil were likely to set the color whereby prime oil would not be obtained from prime seed as it would be if it were done by pressing. The cause of the trouble was quickly determined and is acknowledged to be both time and temperature (1).

Different Official Cup Test Refining Rules were provided for the two main grades of cotton oil produced by the hydraulic method in one case and expeller in the other because there was a marked difference between oils produced by the two methods. There was also a difference between hydraulic oils, one being what is called regular, and the other, slow-break. The slow-break and the expeller methods were very similar except that the Official Cup Refining method specifies that slow-break oil be stirred for 20 minutes and expeller oil be stirred for 12 minutes in the hot and a higher Baumé caustic be used on the expeller oil. The "Slow-Break" method gives to some hydraulic-type cooked, expeller oils, fictitiously low refining losses.

Recently a change in the heating, drying, and cooking procedure has altered the nature of expelled cotton oil as previously known. Perhaps the main reason for the difference now is that the hydraulic cooking process is used. Moisture is added, and the temperature is brought up, perhaps under very slight vapor pressure, and then the moisture is evaporated to the right degree for mechanical expelling. The cookers employed were identified as 3- to 5-high stack. They are chambers provided with agitators where the cooking of the meats can be controlled as to time, temperature, and evaporation of moisture. It is evident, by comparison with the prior expeller or cold-pressed method, that these two expeller oils are different. The short cooking period formerly used was really nothing more than a warming-up to evaporate the moisture so that the expeller would properly operate against friction due to low moisture content of the cottonseed meats, and the resultant oil contained considerably more coloring matter, such as gossypol and material of like nature, but had a comparatively small amount of phosphatides. This change has produced an oil that is more like the hydraulic than the original screw-pressed oil.

In addition to this, there has been a turn to expelling or pre-pressing prior to solvent extracting whereby in the case of cottonseed oil, about two-thirds to three-fourths of the oil is removed in the mechanical pressing operation and one-third to one-fourth by solvent extraction. The method is of course economical and attractive for the reason that considerably less solvent is employed in this two-stage operation and the wear and tear on the mechanical presses is minimized, but the coloring matter is concentrated in the solvent-extracted portion and the color of this type of oil is more resistant to the usual refining methods. The refining losses seem to be excellent however, especially if the slow-break method is specified.

Table I shows a comparison of pre-pressed and solvent extracted crude cottonseed oils as to calculated phosphatides (%P x 26), cup color, cup refining loss, and theoretical or Wesson loss. These oils were made from West Texas seed, which normally produces oils of high color in comparison to the other parts of the cotton belt.

It is interesting to note that oils from the pre-pressing stage are usually much lighter in bleach color and definitely show that the solvent stage is burdened with the problem of removing the residual oil, without increasing the color over that of the pre-pressed portion.

THE soda ash refining process, which is a two-stage sodium carbonate and sodium hydroxide refining treatment, employs in the second step a highly concentrated caustic soda for the color reduction (2). The operation is quick and does not expose the strong caustic to the neutral oil for a time sufficient to cause saponification losses. At the same time the employment of a water-flush type of centrifuge permits a small quantity of strong caustic soda to be used and prevents emulsification of free oil in the soap produced and stratification or salting out of the soap by completely dissolving it in water. An example of the effect on color reduction, by varying the strengths of lye but keeping the quantity of NaOH constant, on cottonseed oil that has been previously neutralized with sodium carbonate is given in Table II. It is therefore possible to obtain colors lighter than cup bleach colors by employing the right strength of lye and proper mixing in the second step of the soda ash process, with insignificant loss of neutral oil free or saponified.

TABLE I

Crude Cottonseed Oils, West Texas, Year 1953 — Pre-Pressed and Solvent Extracted

No.	Crude Cottonseed Oil	H_2O (Volatiles) (at 105°C.)	F. F. A.	Phosph. (%Px26)	Wesson Loss	Cup Tests		
						Refining Color		Bleach
						Loss	35 Y–	20 Y–
		%	%	%	%	%		
6403	Mill "L"—Pre-Press Oil	0.27	1.8	2.05	3.19	6.0	6.5 R	2.7 R
6404	Mill "L"—Solvent Oil	0.18	1.4	2.65	2.87	9.0	7.6	3.1
5887 6076 5970	Mill "L"—Pre-Press Oil	0.41 0.21 0.20	1.6 1.4 1.7	1.89 3.17 2.57	2.96 2.92 3.81	6.7 6.2 8.4	6.7 7.5 4.3	2.3 2.8 2.2
5888 5971 6077	Mill "L"—Solvent Oil	0.01 0.08 0.37	1.2 1.5 1.7	2.63 3.20 3.25	2.91 3.71 4.41	8.4 10.7 10.9	5.6 5.1 7.2	2.5 3.3 2.5
6396	Mill "P"—Pre-Press Oil	0.12	1.2	1.92	1.94	6.3	6.2	2.6
6397	Mill "P"—Solvent Oil	0.13	2.1	2.11	3.42	10.5	14.3	8.9
5902 5974 6047	Mill "P"—Pre-Press Oil	0.11 0.07 0.10	1.0 1.4 1.3	1.77 2.42 1.76	1.98 2.43 2.20	4.8 7.4 6.1	4.6 6.2 7.1	1.2 1.5 3.4
5901 5975 6048	Mill "P"—Solvent Oil	2.20 0.14 0.31	1.5 1.1 1.2	3.61 2.57 3.07	5.87 2.17 3.54	13.3 8.3 9.5	12.0 14.7 18.6	7.4 7.5 11.9
6399	Mill "PH"—Pre-Press Oil	0.24	2.7	1.82	4.30	6.1	7.9	2.1
6400	Mill "PH"—Solvent Oil	0.22	2.8	1.72	4.52	8.7	6.6	3.3
5918 6006 6125	Mill "PH"—Pre-Press Oil	0.09 0.08 0.42	2.5 1.6 2.2	1.80 1.43 4.89	3.78 2.35 9.26	7.8 5.9 15.0	6.2 4.4 9.3	2.3 0.9 2.5
5917 6007 6126	Mill "PH"—Solvent Oil	0.33 0.21 0.22	2.8 1.6 1.9	1.77 1.24 2.11	4.49 2.40 3.18	10.8 8.4 9.0	8.8 6.2 7.4	3.7 1.8 3.5
6395	Mill "BH"—Pre-Press Oil	0.11	2.8	1.09	3.76	6.0	6.4	1.9
6394	Mill "BF"—Solvent Oil	0.12	3.4	1.54	4.49	9.9	7.2	2.2
5925 6127	Mill "A"—Pre-Press Oil	0.17 0.20	1.3 1.8	2.55 2.18	2.82 3.82	9.0 7.1	8.5 8.5	4.4 5.2
5926 6128	Mill "A"—Solvent Oil	1.01 0.28	1.9 1.8	1.38 2.39	6.57 3.96	11.3 9.6	11.5 8.4	6.8 4.2

A mixer that has proven effective in the second step is illustrated in Figure 1. It is unique in that comparatively little horse-power is required for the very effective mixing which results. There are six shear rings containing 24 vanes each, in which an impeller with blades revolves 640 r.p.m., which gives 97,000 shear points per minute (6 × 24 × 640). A shear point is that instant during which the impeller tip passes one vane in the shear ring. The mixer requires less than 5 h.p. for a four-tank car per 24-hour-day capacity.

TABLE II

Laboratory Re-Refining of Cottonseed Oil from First Step of Soda Ash Process. Two Batches Oil from Primary Centrifuges Re-Refined with Lyes of Various Strengths in High Speed Mixer, 2 Minutes

Lye Used	Color		Bleach	
	A	B	A	B
2.5% 20°Be'........................	8.6 R	9.7 R	3.0 R	2.7 R
1.82% 26°Be'......................	7.7 R	8.7 R	2.5 R	2.0 R
1.53% 30°Be'......................	7.1 R	7.8 R	2.1 R	1.8 R
1.24% 36°Be'......................	6.4 R	7.7 R	1.9 R	1.4 R
Official Cup Test Crude Cottonseed Oil..........	8.2 R	12.0 R	3.5 R	5.0 R

TABLE III

Effect of Varying Strengths of Caustic Solution on Color Reduction in 2nd Step of Soda Ash Refining

Crude Cottonseed Oil..	7.1% F.F.A.
Cup Color..	18.2 Red
Cup Bleach..	5.7 Red
Cup Loss..	18.3%

Neutralized Primary Oil from Soda Ash Refining (first step)
Re-Refine—2 Minutes High Speed Mixer (second step)

Caustic	Dry NaOH	Color	Bleach
2.5% 20°Be'..............................	(0.35%)	13.2 R	5.5 R
1.82% 26°Be'............................	(0.35%)	12.9	4.6
2.5% 30°Be'..............................	(0.59%)	12.1	4.3
1.67% 30°Be'............................	(0.39%)	13.8	4.1
2.5% 36°Be'..............................	(0.75%)	10.4	2.8
1.32% 36°Be'............................	(0.39%)	11.9	2.8

The results of another study of the effect of concentration of NaOH on the color and bleach of cottonseed oil are given in Table III. The oil that had a cup bleach of 5.7 red was treated after soda ash neutralization in the first step, with varying strengths and amounts of caustic soda solution.

The bleach color was progressively lower as the strength of caustic increased; at 36°Bé NaOH level 1.32% of this solution gave the same bleach color as 2.5%. The comparative effect of dissolving this soda ash neutralized oil from the first step in hexane to make a 50% miscella and then re-refining with caustic soda solution of different strengths in a high speed mixer (Waring blendor) for 4 minutes is shown in Table IV.

It is interesting to note that the treatment of the straight oil with 2½% of 20°Bé lye, gave a color of

TABLE IV

Crude Cottonseed Oil: Re-refining Cottonseed Oil in Hexane Same as in Table III

50% Primary Oil from Soda Ash Refining Mixed in Hexane 50% and Re-Refined with Various Strengths of Caustic Solution in High Speed Mixer for 4 Minutes

Caustic	Dry NaOH	Color (Solvent-free basis)
A. 2.5% 20°Be'........................	(0.35%)	21.6 R
B. 2.5% 26°Be'........................	(0.48%)	16.4
C. 2.5% 30°Be'........................	(0.59%)	13.6
D. 2.5% 36°Be'........................	(0.75%)	14.6

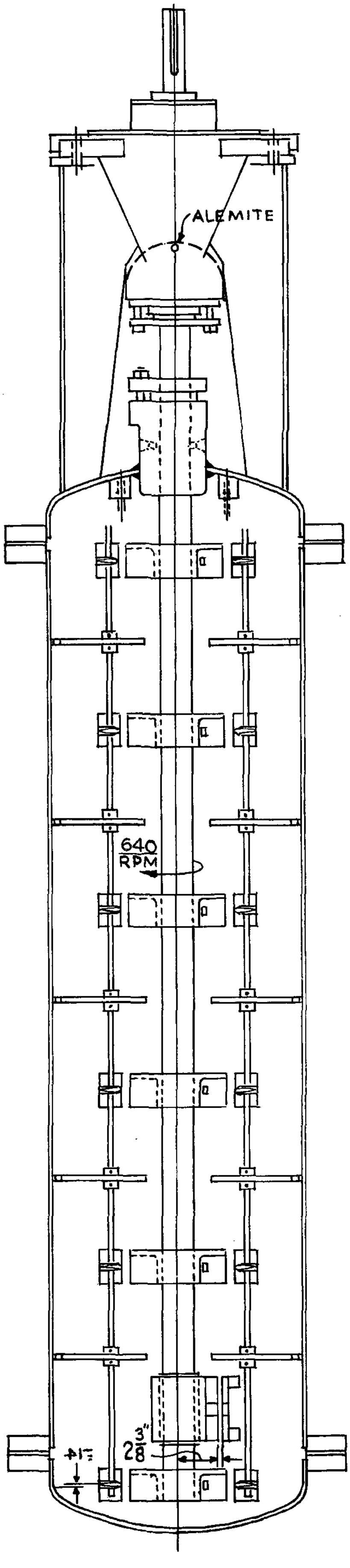

Fig. 1.

13.2 red, but when refined in the 50% oil miscella with the same quantity and strength of lye, the color was 21.6 red (Table IV). But this refined oil miscella, when washed with 3% of water, came down to an oil color of 13.1 red, showing that hexane solvent holds back color in solution, preventing the caustic from dissolving this out along with the other coloring matter and soap.

A comparison of the effect of water-washing a miscella treated with caustic soda solution is shown in Table V. It is apparent that 3% of water is sufficient, compared to 10%, to remove the color remaining after caustic miscella re-refining. This washing step should be adopted for miscella refining, being relatively inexpensive. Because only 3% of water is required, it offers the advantage of having very clean miscella going to the final evaporators and stripping column with little loss of hexane in the waste water.

TABLE V

Crude Cottonseed Oil: Effects of Re-refining Cottonseed Oil in Hexane Same as in Table III

50% Primary Oil from Soda Ash Refining Mixed in Hexane 50% and Re-refined with Various Strengths of Caustic Solution in High Speed Mixer for 4 Minutes

Re-refined Miscellas Washed with Various Amounts of Water—Effect on Color

Caustic	Color (Solvent-free basis)	% Water Added	Color of Washed Oil (Solvent-free basis)
2.5% 20°Be'..........	21.6 R	none	....
2.5% 20°Be'..........	21.6 R	3%	13.1 R
2.5% 20°Be'..........	21.6 R	10%	13.0 R
2.5% 36°Be'..........	14.6 R	none	....
2.5% 36°Be'..........	14.6 R	3%	9.9 R
2.5% 36°Be'..........	14.6 R	10%	9.9 R

The usual oil content of miscella from the average extraction plant is hardly ever in excess of 25% and would probably run on the average less than 20%. Because the trend of extraction in the cottonseed oil industry is toward pre-expelling and solvent extraction combined, it would be to the advantage of such a processor to refine in the miscella the three-fourths pre-expelled portion by diluting the miscella from extraction plant, containing 20% oil, for example, with the pre-pressed oil, which would yield approximately 50% oil miscella. For that reason considerable work has been done and data accumulated on that strength of miscella to show that it is practical to refine miscellas containing as low as 50% of oil. Nevertheless it will be noted by referring to Table VI that the ease of removing color from oil contained in the solvent is roughly proportional to the concentration of oil and that there is an advantage in concentrating miscella to 75% oil instead of 50%. It is also to be pointed out that certain surface active agents may be effective in reducing color in low oil miscellas. There is evidence however that a high strength and high excess of caustic can be used in miscella refining with little loss of neutral oil and thereby produce excellent colors without these agents, especially when the oil in the miscella is kept at a maximum.

It is interesting to note that the 25% oil miscella was hardly affected as to color reduction by caustic soda with an excess equal to what is specified by the Official Cup Refining Tests and is approximately three times as much as would be employed by factory caustic refining.

Because the boiling point of 75% oil miscella is considerably below the danger point of setting color in cottonseed oil, the producer would benefit by concentrating by evaporating miscella to 75% oil content. Nevertheless, as is shown, 50% miscella can be handled with as good color reduction as 75%, provided washing or a surface-active agent is employed, although as Table VI shows it is not necessary to use surface-active agents on a 50% oil miscella. In one case an agent will increase the color while with another it will lighten it only slightly compared to refining without it.

TABLE VI

Miscella Refining—Laboratory Tests

Crude Cottonseed Oil—Solvent Extracted—West Texas Seed
F.F.A. 1.6%—Cup Color: 35 Y—7.6 R—Cup Bleach 3.1 R
Miscella (crude oil + hexane) mixed for 5 minutes

% Crude Oil in Miscella by weight	Lye Used (based on wt. of crude oil)	Additive (based on wt. of crude oil)	Color of Refined Oil (Solvent-free basis)
100% by weight	5.92% 20°Be′	none	6.8 R
75%	5.92% 20°Be′	none	7.9 R
50%	5.92% 20°Be′	none	6.7 R
25%	5.92% 20°Be′	none	too dark to read
75%	5.92% 20°Be′	none	7.9 R
75%	5.92% 20°Be′	0.1%—A	7.6 R
75%	5.92% 20°Be′	0.1%—B	8.4 R
50%	5.92% 20°Be′	none	6.7 R
50%	5.92% 20°Be′	0.1%—A	8.0 R
50%	5.92% 20°Be′	0.1%—B	7.4 R
25%	5.92% 20°Be′	none	too dark to read
25%	5.92% 20°Be′	0.1%—A	too dark to read (175.0 Y-23.0 R)
25%	5.92% 20°Be′	0.1%—B	too dark to read (175.0 Y-27.0 R)

NOTE: A—polypropylene glycol—425.
B—Triton X-100 (octyl phenol polyglycol monoether).

MISCELLA refining is now being practiced on a large scale. The advantage is protection against saponifying neutral oil in the refining step due to the hexane solvent, which permits the use of a very high excess caustic soda to remove more color than is obtained by the cup test on a straight oil after the miscella has been evaporated. Therefore those employing pre-pressing and solvent extraction on cottonseed will find it to their advantage to employ miscella refining in order to be able to use high excesses and high Baumé caustic to improve the color of the miscella oil, which is usually darker than the pre-pressed portion. This can be done with little sacrifice in refining loss. There is the problem of setting color in cotton oil while evaporating the last 15% of the solvent (1). The critical temperature and time at which color is set is 180°F. for 1 hour, or 210°F. for 15 minutes. Another advantage to refining in the miscella is the removal of the "fines," soluble carbohydrates and proteins, which form scale on the evaporator tubes.

The advantages of separating soapstock from miscella rather than from oil without solvent may be seen from the following discussion. According to the Stokes law, the settling rate of a particle is proportional to the difference between the density of the particle and the density of the medium in which it is suspended, divided by the viscosity of the medium.

For example, take a 50/50 oil and hexane miscella, which has a viscosity of 3.65 centipoises at 77°F. When refined with 5.9% of 20°Bé caustic having a sp. gr. of 1.16, the soapstock produced by a refining loss of 5.2% will have a sp. gr. of 1.05. The miscella in which this is suspended will have a sp. gr. of .79. This, by applying the formula, gives a settling rate factor of 0.071. If the same crude oil without hexane is refined with 5.9% of 20°Bé caustic at 122°F., refining loss of 9%, the sp. gr. of the soapstock is 1.02, and the sp. gr. of the refined oil .90. The viscosity of the refined oil is 26.35 centipoises. The settling rate factor is 0.0048. This means that a centrifugal employed in miscella refining theoretically could separate and settle out the soapstock 15 times as fast from 50/50 oil-hexane miscella at 77°F. as when operating on soapstock and oil at 122°F. without hexane. The practical tests show that one and one-half times the centrifuge straight oil capacity is safe to accept for miscella.

Refining Fatty Oils with Ammonia

A new and most interesting process has been developed and tested, the Clayton Ammonia Refining Process. For certain crude oils a water solution of ammonia, about 14% NH_3, is used as the neutralizing refining agent which can be evaporated subsequently from the ammonia soapstock and re-used as the neutralizing agent. Only about 20% of the ammonia required for refining is needed as make-up in re-using the recovered solution.

An unusual by-product (soapstock) results from this process, which is similar to water-degummed lecithin, but the acetone insoluble (phospholipid) portion is higher. A typical analysis of such a moisture-free product from the ammonia refining of an extracted crude soya oil is 75% acetone insoluble and 25% acetone soluble. The soluble portion analyzes 8% F. F. A. and 17% free oil, based on the weight of the dried product.

Water-degumming, where substantially all the phosphatides are removed from the crude oil, yields a product containing (moisture-free basis) 62% acetone insolubles and 38% acetone solubles, but the F. F. A. of the crude oil treated remain in the oil. The analysis of the acetone soluble portion usually runs 34% oil and 4% F. F. A. The advantage of producing ammonia soapstock is readily seen. The oil and fatty acid portion is unaltered. The phosphatide portion, also substantially unaltered, finds great possibilities as a source of inositol and choline. The fact that it has these nutritive components and fat provides a valuable additive to extracted meals. Ammonia refining eliminates acidulation of soapstock and shipping the non-acidulated by-product from caustic refining, containing about 50% water. A neutralized oil is produced which requires only a quick caustic wash followed by the usual washing and drying steps, or the caustic wash may be eliminated for certain end-uses of the oil. Ammonia refined oil has been bleached and deodorized into edible oil, and keeping tests of it have been made. The quality determined in this manner, showed it to be equal to, or better than the standard caustic refining and other steps normally employed in the manufacture of edible oils.

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