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Continuous Purification and Acidulation of Vegetable Oil Soapstock

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SOAPSTOCK from vegetable oil refining usually presents either a disposal problem for the refiner or a processing problem for the user, and frequently both conditions prevail. A few years ago an excess of supply over demand permitted the buyer to choose his sources on the basis of quality. More recently, shortages have favored the refiner with a higher market price, but they have also increased the buyer's problem of quality control, particularly in the production of fatty acids.

Several years ago work was started on methods of purifying soapstock; results of laboratory and pilot plant studies have been reported previously (1). It was found that the nature of the impurities in vegetable oil foots rendered them resistant to treatment by acids as in normal acidulation. Reaction with a small excess of caustic above that theoretically needed for saponification could, with prolonged boiling, produce a fully saponified soap of higher TFA than the foots but with erratic and often limited reduction in impurities. Strong caustic however attacked the gums and made them at least partially soluble in 5 to 10% aqueous caustic solution. At this concentration a soap phase of 40–55% TFA could be centrifugally separated, and the majority of the impurities or their degraded products discharged with the lye stream. Oxidized Acids, as determined by A.O.C.S. Tentative Method G3-53, and other more or less insoluble impurities could be reduced to 5% or less in Black Acids produced from the soap. Laboratory distillations showed marked reduction in still losses and greatly increased color stability for these purified fatty acids without the necessity of Twitchell or pressure-splitting.

Batch acidulation of the purified soap was not always readily accomplished, and some of the usual plant acidulation problems were still present. The fatty acids, for example, were discolored by contact with strong mineral acid for extended periods, and with some stocks a fairly long boil was necessary to complete acidulation. Also, with most soaps, breaking of the interfacial emulsion or curd was still slow. The laboratory study was therefore extended to include methods of continuous acidulation of the purified soap. The order and rate of addition of the reactants had no consistent effect on the rate of reaction. It was found however that proper dilution of the mineral acid plus addition of a small amount of one of several commercial dispersing agents caused a fast and complete acidulation reaction with rapid breaking of the emulsion. The resulting fatty acid phase was clean and brown in color. In a commercial installation of the process it became refinery practice to call these treated fatty acids Brown Acids to distinguish them from the Black Acids made by standard acidulation of soapstock, this terminology will be used here for convenience.

Process Flow Sheet

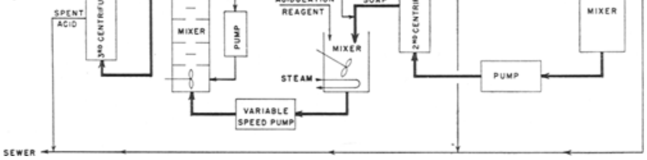

FIG. 1. Continuous purification and acidulation of soapstock.

A full scale continuous plant incorporating three stages was installed at the Opelousas Oil Refinery in Opelousas, La. This unit was operated on an experimental basis while testing different types of mixing equipment, pumps, and control methods to complete the scale-up from pilot plant for soapstock purification and from laboratory data for the acidulation. The final process is outlined in Figure 1. Soapstock is withdrawn from the refinery receiving tank and metered to the system by a variable speed gear pump. Immediately before the mixer 50% caustic and hot water, regulated by rotameter, are added to the line. The mixer is compartmentized and agitated; the bayonet-type of steam heaters maintain temperature with a controller on the out-going mix. The hot mix passes downward through a hold-up tank and is separated into soap and pitch water in the 1st stage centrifuge. The soap, usually at 35–50% TFA, is diluted in the covers of the centrifuge with hot water and drops into an open tank where it is grained by 20% brine added through a rotameter. Agitation is accomplished by an over-size gear pump and a high rate of recycle. A regulator in the recycle line adds live steam to maintain a temperature of 170–185°F. A weight controller on the tank diverts feed to the 2nd stage centrifuge, where soap and pitch water are again separated.

The purified soap at 50–62% TFA is diluted with hot water in the covers of the 2nd stage centrifuge and drops directly into an agitated open tank with steam coils. After heating to about 180°F. and blending with 2.5% solution of a dispersing agent, which is added by rotameter, the mix is fed by a variable speed gear pump to the bottom of the acidulation tower. The 66° Bé. sulfuric acid is diluted to about half strength by hot water with rotameter regulation before being pumped to the bottom of the tower. Generally no heat is needed in the tower, but it can be supplied by live steam if required. A Monel metal or plastic-lined tower is necessary with alternating disc and donut Monel baffles spaced every 6 in. The overflow from the tower is fed directly to the 3rd stage centrifuge, where it is separated into Brown Acids and spent mineral acid. The latter partially neutralizes the 1st stage pitch water in a skim tank before discharge to sewer.

During scale-up from the pilot plant two important changes were made in the 1st stage. Originally soapstock was blended with water and heated in an open tank before addition to the mixer; changes in soapstock viscosity required compensating changes in water addition. With the shift to closed feed the system became relatively insensitive to viscosity changes.

The hold-up tank after the 1st-stage mixer was a necessary addition to the process. It was a vertical tank about 29 in. in diameter and 12 ft. high with no baffles, heating, or agitation. Some soapstocks were encountered which appeared to be grained in the mixer alone but which had so strong a tendency toward emulsification that a clean centrifugal separation could not be obtained. When these inadequately treated stocks were passed through a quiescent hold-up tank, a stable grain resulted probably because of the increased reaction time and further degradation of the emulsifying impurities. Agitation of the hold-up tank decreased its effectiveness considerably. Even stocks that could be handled directly from the mixer benefited by the additional hold-up time. In most cases caustic requirements were reduced, and the quality of the soap was improved. An outstanding example is shown in Table I for stock from soda ash-refined hydraulic cottonseed oil. Salt was used in this run as an auxiliary graining agent but was held constant during the run. The results were similar in other runs without salt. In Condition A of Table I the hold-up tank was not used while in Condition B the same mix was passed through the hold-up tank. Condition C represents a reduction in NaOH, using the hold-up tank, while D shows that the same mix as C without the hold-up tank was insufficiently grained to give a split in the centrifuge.

TABLE I

Effect of Holdup Tank on First Stage Soap

Sample Source	Holdup Tank Time (min.)	TFA (%)	OA/BA[a] (%)	Concentrations in Pitch Water (%)	
				NaOH	NaCl
Soapstock Feed	....	15.9	7.6	....	....
Condition A	0	21.8	7.4	9.6	6.3
Condition B	26	31.9	5.9	10.1	6.2
Condition C	29	33.5	5.8	6.8	6.6
Condition D	0	(Grain too closed to split)			

[a] OA = Oxidized Acids, BA = TFA + Oxidized Acids.

Process Conditions

The effects of the process variables in the 1st stage of the full scale plant bore out the conclusions reached in the pilot plant although the sensitivity to changes in soapstock feed or process conditions was very much reduced by introduction of the hold-up tank. In general, 1st-stage temperatures were kept at 200°–210°F. to maintain a high soap TFA. Low ratios of soap phase to lye phase gave slightly better quality soap, but high ratios gave better economy. A compromise ratio of about 1.0–1.2 lbs. of soap produced per pound of pitch water was set as the nominal operating range. Operation with the minimum caustic concentration necessary for graining and centrifugal separation tended to decrease TFA and to improve slightly the removal of impurities. Any caustic addition higher than the minimum produced satisfactory soap with little effect from changing the lye concentration. Generally the concentration of caustic in the 1st-stage pitch water was 7–12% with total solids at 18–32%. Partial replacement of 1st-stage caustic with another graining agent, such as sodium chloride, reduced the soap quality. TFA in the pitch water averaged 0.1% for expeller or extracted oil soapstocks and 0.3% for hydraulic stocks with little effect from the type of refining. Material balances on the NaOH, allowing for saponification of the neutral oil content of the soapstock, indicated that roughly a quarter of the caustic might be used in reaction with the impurities.

TABLE II

Effect of 3rd Stage Spent Acid Concentration

Conc. of H_2SO_4 in Spent Acid (%)	Brown Acids Acid Value	Distilled Acids	
		Still Loss (%)	24 hr. Color (Gardner)
5.2	190	24.8	3 D
3.8	190	26.0	3 L
1.9	188	26.4	3
1.2	188	28.0	5

The 2nd, or washing, stage was relatively insensitive to process variables. It was necessary to maintain a temperature of 170°–185°F. as lower temperatures produced foamy emulsions instead of clean grains. The soap/pitch water ratio was in the range of 1 to 2 lbs./lb. with NaCl in the pitch water at 6–8%, total solids at 15–20%, and TFA averaging 0.2%.

The variables of the 3rd, or acidulation, stage were most interesting as the effect on Brown Acid quality was quite marked. The result of varying the mineral acid concentration is shown in Table II.

It is seen that still losses decrease and acid values increase as the acid concentration increases, probably due to more complete reaction and better removal of residual impurities. Color is high at low acid concentration where reaction may be incomplete. After passing through a minimum at 3–4% H_2SO_4, color tends to increase for higher acid concentrations, where "burning" may occur. Plant operation at about 4% H_2SO_4 in spent acid is very satisfactory.

The acidulation temperature has considerable effect, as shown in Table III, for a set of runs at about 4.5% spent acid and 10-min. hold-up time in the acidula-

TABLE III

Effect of Acidulation Temperature

Acidulation Temperature (°F.)	Brown Acids Acid Value	Distilled Acids	
		Still Loss (%)	24 hr. Color (Gardner)
170	190	25.2	2
180	188	23.8	3
193	188	23.8	3
200	....	23.4	3 D
215	189	26.0	4

tion mixer. At 170° the increased still loss shows incomplete acidulation although the high acid value and good color indicate that the cleaner acids in the mix may react more rapidly. At 180° and 193° the still losses are low and color is good, but at 200° and above color is adversely affected. At 215° polymerization increases the still losses.

Residence time in the acidulation mixer was also tested over the range of 9 to 15 min. as shown in Table IV; still losses and color both decreased somewhat with increased hold-up time. These results together with the temperature data indicate that the best operating condition for the acidulation mixer is 170°–175° at 15 min. hold-up time with satisfactory operation up to 195° at 10 min.

TABLE IV

Effect of Residence Time in Acidulation Mixer

Residence Time (min.)	Brown Acids Acid Value	Distilled Acids	
		Still Loss (%)	24 hr. Color (Gardner)
14.5	189	21.8	3
10.6	188	23.8	3
9.2	188	24.6	3 D

It should be noted that figures for still losses are based on laboratory distillations. Distillation results from different laboratories, using the same still and apparently the same procedure, have differed appreciably although the data from any one laboratory have usually been consistent. For example, the average still loss on the first five tankcars as determined by the buyer was 17.1% while the average from production control tests was 20.0%, about 3% higher. For consistency as well as availability, production figures are used throughout.

Reagent consumption is always an important economic consideration. Data are available from spot checks twice a day during the first six weeks of regular production following the experimental operation. The average results are given in Table V in pounds of reagent per pound of Brown Acids produced. Of the four reagents, caustic was the only one that varied appreciably with type of soapstock.

TABLE V

Reagent Consumption in Production Runs

Process Stage	Reagent	Reagent Conc.	Usage in lb./lb. of Brown Acids
1	NaOH	100%	0.31
2	NaCl	100%	0.06
3	H_2SO_4	66° Bé.	0.32
3	Dispersing Agent	100%	0.0024

The unit operated satisfactorily for Brown Acid rates ranging from 6 to 16 lb./min. The 1st stage showed a decrease in soap quality at rates over 45–50 lb. per min. of soapstock, but these differences were not apparent in the Brown Acids.

Analytical data are available for the 23 tankcars of Brown Acids produced to date, and these are summarized in Table VI. Laboratory distillation losses as determined by the buyer are available for a number of cars and these range from 14–22%.

TABLE VI

Summary of Opelousas Brown Acid Production

	Range	Average
Brown Acids:		
Moisture, %	1.3– 4.6	3.0
TFA, %	91.0– 94.3	92.9
Unsaponifiables, %	1.7– 4.5	3.2
Acid Value	184 –191	188
Iodine Value	99.6–105.0	102.2
Laboratory Distilled Acids:		
Still Residue, %	18.0– 24.0	21.0
Gardner Color	1 D–2	2 L
24-hr. Gardner Color	1 D–5 L	2

The data in Table VI on distilled acid colors were obtained on a middle cut amounting to 50% of the Brown Acids still charge. The 24-hr. color reversion on this cut at 95°F. was about one-third of a Gardner color unit so that the average darkening for production was from 2L to 2. On recent production an accelerated color stability test was also made by holding a sample at 250°C. for 30 min. These results are available for five tankcars as shown in Table VII.

TABLE VII

Results of Accelerated Color Stability Test
Gardner Color of 50% Color Cut

Fresh	24 hr. @ 95°F.	After 30 min. @ 250°C.
2 L	2 L	4 L
2 L	2	4 D
2 L	2 L	5
1 D	1 D	6
2 L	2	5 L

Summary

In summary, the results from full-scale continuous production indicate that all types of cottonseed soapstocks are sufficiently upgraded by treatment with strong caustic and graining and washing to permit subsequent acidulation. At 175°–195°F., in the presence of a dispersing agent with spent mineral acid at about 4% H_2SO_4, acidulation of purified soapstock yields a clean, brown, fast-breaking fatty acid phase with acid value about 188, unsaponifiables about 3%, and an Oxidized Acids content of 3–5%. In laboratory distillations, still residues are usually in the range of 18–23% with a 24-hr. Gardner color of about 2 on the color cut.

Acknowledgment

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REFERENCE

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