Summary

An investigation of the removal of soap from neutralized vegetable oils by washing with water has shown that some oils are obtained practically soap-free after only one water wash whereas the soap in other oils cannot be removed even by repeated washing. Coconut, palm, and olive oils are easily washed whereas linseed and rapeseed oils are not. Peanut, sunflowerseed, soybean, and cottonseed oils are sometimes washable and sometimes not.

With unwashable oils different methods for soap determination give inconsistent results because calcium and magnesium soaps, or other naturally-occurring compounds of these metals, are not determined to the same extent by these methods. Calcium and magnesium in the crude oils are probably combined with phosphatides or other lipids and remain to some extent in this state after neutralization. Calcium and magnesium present as soaps or as any other compound may be detected easily in crude, neutralized, and washed oils by the titration method of Wolff.

Washability of neutralized oils may be improved in a number of ways; the most efficient is pre-treatment with concentrated phosphoric acid or re-refining with a mixture of sodium hydroxide and sodium carbonate. Either of these treatments can be applied in batch or continuous refining processes. To prevent contamination of washable oils with calcium and magnesium, soft water should be used for washing and in preparation of refining solutions.

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[Received February 2, 1956]

The Destruction of Gossypol in Cottonseed Oil Soapstock by a Heat Treatment[1]

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THERE IS A NEED to find uses for the excess supplies of oil soapstocks. Approximately 120 million pounds of cottonseed oil soapstock are produced annually in this country (reported as refining loss). The market price of cottonseed oil soapstock, when salable, is often insufficient to cover transportation costs. Some refiners have been forced to discard this material, and even its disposal may prove troublesome at times by reason of conservation laws. Examined for the specific case of cottonseed oil soapstock, many proposed uses aimed at an increased utility for this material would benefit by a reduction in the amount of or the outright destruction of the gossypol contained in soapstock. The gossypol content of cottonseed oil soapstock may vary from 0 to approximately 4%. Samples of alkaline soapstock analyzed in our laboratories exhibit a range from a few tenths of 1% to nearly 4%. Acidulated soapstocks show a range of from substantially 0 to 6%. All of our gossypol analyses employ the *p*-anisidine method.

The efficient preparation of considerable amounts of degossypolized soapstock for evaluation purposes necessitated the designing, construction, and operation of a continuous, pilot-plant scale, degossypolizing apparatus. The apparatus based on previously reported laboratory data (1) and its operation is the subject of this paper.

Apparatus

The pilot-plant apparatus is designed to process approximately 1.88 lbs. or 0.25 gal. of raw alkaline soapstock per hour at temperatures of 212°–215°C. and pressures of 290–300 lbs. p.s.i. Figure 1 is a photograph, and Figure 2 a flow diagram of the apparatus. Alkaline soapstock is forced through the system continuously while being subjected to the heat treatment. The pressures developed are the result of heat-treating temperatures and are not in themselves essential for the destruction of gossypol. The heated,

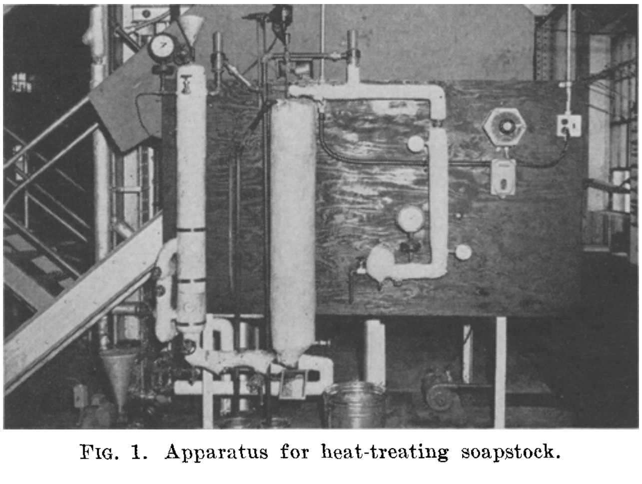

FIG. 1. Apparatus for heat-treating soapstock.

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[1] Presented at the fall meeting of the American Oil Chemists' Society, Chicago, Ill., September 24–26, 1956.

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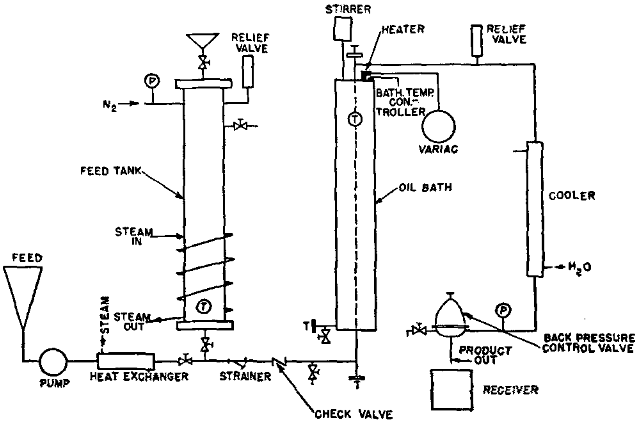
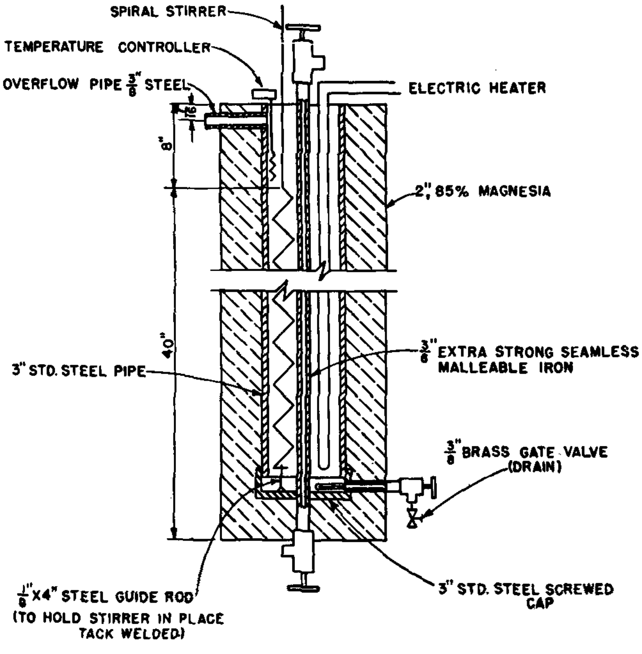


FIG. 2. Flow diagram of heat-treating apparatus.

alkaline soapstock (approximately 50–60% water) is pressurized so that high temperatures can be attained without losing, as a result of water vaporization, the liquid physical characteristics of the soapstock. The heat treating system comprises a holding tank wrapped with steam coils; a high-pressure, positive-displacement, diaphragm pump; a heat-treating tube through which the soapstock is forced; and a spring-loaded back pressure valve for control of the system pressure. Simple, pipe-jacketed, heat exchangers are employed for preheating the untreated soapstock and for cooling the treated soapstock. The holding tank is a 4-ft. length of extra strong, seamless, 3-in. steel pipe with a pipe cap on each end. The pump feed is of variable volume capacity. Either the pump or the holding tank containing nitrogen gas under pressure may be used to force soapstock through the system. Figures 3 and 4 show the structural details of the heat-treating tube and of the oil bath that is used to heat the tube. The bath is heated electrically with a 2,000-watt immersion heater, and the temperature is controlled with a bimetallic thermoregulator that operates through a relay. The heat-exchange surface of the treatment tube immersed in the oil bath is .0082 sq. ft. Relief valves are installed as a precautionary measure. All piping in the system is extra strong, seamless steel, and all the fittings are rated for service at 300 lbs. p.s.i.

Operational Details

Experimental treatments were made on various types of soapstock (soda ash-refined and caustic-refined). During the initial experimental runs, soapstock was forced through the system from the holding tank by means of the pressure exerted by cylinder gas (N_2). Gas pressures were adjusted by reference to steam tables since the temperature and pressure relations for raw alkaline soapstock closely approximate those for water. However use of the holding tank and gas pressure for feeding soapstock through the apparatus proved somewhat troublesome. Uneven flow, and as a consequence thereof localized overheating, caused the development of pressures within the heat-treating tube that exceeded the controlled nitrogen gas pressure. The excessive pressures, produced periodically, in turn caused spasmodic ejection of soapstock not uniformly heat-treated. In addition, toward the end of each batch run there was a tendency for small quantities of the nitrogen gas under pressure to by-pass the viscous soapstock and enter



NOTE: TWO BRACKETS TACK WELDED TO PIPE 6" FROM PIPE ENDS. TEES AS CLOSE TO BATH AS POSSIBLE.

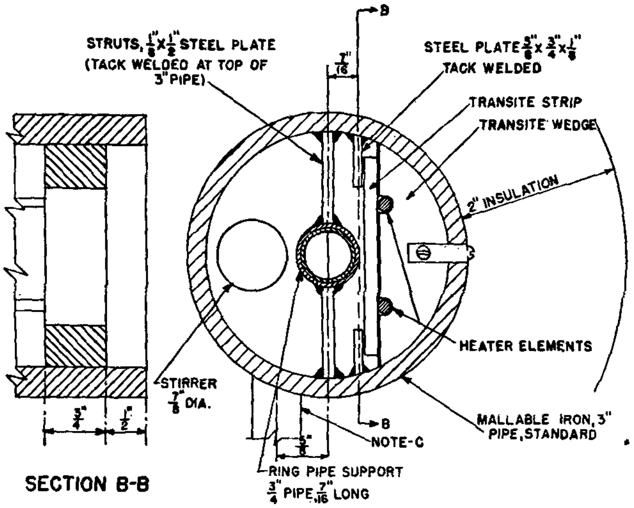
FIG. 3. Cross-section of oil bath.

TABLE I

Processing Data

Type Soapstock	Rate lbs./hr.	Holding time[a] min.	Pressure lbs./sq. inch	Soapstock Temp. °C.		Analyses			
				In	Out	H_2O %	Total Gossypol %	Free Gossypol %	Total Fatty Acids %
Na_2CO_3,[b] I	Untreated					52.67	0.77	0.23	30.2
	7.43	1.41	275	200	212	65.72	0.16	0.10	20.5
	5.51	1.90	275	200	212	65.75	0.08	0.07	20.2
	1.88	5.51	275	200	211	69.57	0.04	0.03	18.9
Na_2CO_3, II	Untreated					......	2.27	1.85	......
	2.87	3.64	315	175	210	66.0	0.07	0.06	......
	2.75	3.81	290	175	210	60.0	0.09	0.07	......
NaOH	Untreated					59.37	0.62	0.32	27.90
	5.49	1.90	268	155	210	53.52	0.13	0.11	31.08
	4.70	2.22	275	150	211	54.83	0.10	0.09	30.20
	3.86	2.71	270	140	210	55.73	0.07	0.06	29.52
	2.55	4.1	268	170	210	57.47	0.05	0.04	28.76

[a] Holding time in 3.5 ft. of the heat treating tube.
[b] Water added before treatment.



NOTE C: SLEEVE END FITTING ⅜" X 2" FOR DIAL THERMOMETER LOCATED 7" FROM TOP OF BATH.

FIG. 4. Top view of oil bath.

the heat-treating portion of the system. This likewise caused intermittent ejection of soapstock that was not uniformly heat-treated. By use of a positive-displacement, diaphragm pump to force the soapstock through the system these difficulties were avoided. Rates were determined by collecting and weighing the heat-treated product.

Table I is a compilation of several test runs in which the soapstock passed through the apparatus once. Total and free gossypol were reduced to values as low as 0.03%. Cottonseed oil soapstock passed through the apparatus with a holding time of approximately 12 min. (attained by recycling treated material) showed a total gossypol content of 0.003%. Reduction of gossypol is dependent upon the holding time in the apparatus, the temperature of the heat treatment, and the type of soapstock being treated (1). Total fatty acid content of the soapstock is unaffected by the heat treatment. It is of some interest to note that the free and total gossypol content approached a common value, following heat treatment, despite initial differences.

Summary and Conclusions

Successful operation of the apparatus, as described in this paper, was conducted at rates of feed that ranged from 1.89 to 5.51 lbs. per hour. The data show that cottonseed oil soapstock can be heat-treated continuously on a pilot-plant scale so that both the free and total gossypol content, as measured by the *p*-anisidine method (2, 3), are reduced to values as low as 0.003%. In the work reported, the heat transfer medium was oil, heated electrically. Commercially a direct, gas-fired, heat exchanger would be more practical. These experiments indicate that additional work on a larger or plant scale is justified, provided, of course, that the marketing economics involved are favorable.

Acknowledgment

The authors take this opportunity to express their appreciation to H. L. E. Vix of the Engineering and Development Section and L. A. Goldblatt of the Oilseed Section for technical assistance and to V. Cirino and H. P. Pastor of the Analytical Section for the analytical data reported.

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[Received July 30, 1956]

Report of F.A.C. Monoglyceride Subcommittee—1956

THE MONOGLYCERIDE SUBCOMMITTEE of the Fat Analysis Committee was established in 1953 for the purpose of selecting a method for the determination of monoglycerides. The determination of monoglycerides is based upon the original work of Malaprade (1) on oxidation of polyalcohols. Fleury and Paris were the first to report on the reaction of periodic acid on glycerol phosphoric acid, a compound similar to the monoglycerides. The first method for fatty acid monoglycerides was reported by Pohle, Mehlenbacher, and Cook (2). This method was improved by Handschumaker and Linteris (3), and further improvement was made a little later by Pohle and Mehlenbacher (4) and by Krutz, Segur, and Miner (5).

Three methods have been tested comparatively by the subcommittee:

1. *Miner Method* (5). The sample is dissolved in a solution of 5% dimethylformamide in chloroform. The total monoglyceride and glycerol are determined on a 25-ml. portion by oxidation with a methanol solution of periodic acid. When the reaction is complete, a solution of sodium bicarbonate and potassium iodide is added, and the liberated iodine is titrated with a standard sodium arsenite solution, using starch indicator. The glycerol is determined by adding 100 ml. of water to the 25 ml. of the chloroform solution, then 25 ml. of an aqueous periodic acid solution. The monoglyceride is calculated from the difference in the titration for total monoglyceride and glycerol and the titration for the glycerol.

TABLE I

Repeated Analysis of the Same Sample

	Mean	Standard deviation	Coefficient of variation
Miner Method			
1954	38.5	0.41	1.07
1955	38.7	0.92	2.37
1955 (known)	38.6	0.30	0.78
1956 (known)	38.6	0.20	0.52
1956	38.7	0.62	1.60
Average	38.6	0.45	1.27
Extraction Method			
1954	38.4	0.65	1.69
1955	38.6	0.44	1.14
1955 (known)	38.2	0.39	1.02
1956 (known)	38.4	0.25	0.65
1956	38.4	0.41	1.06
Average	38.4	0.43	1.11
Partition Method			
1954	38.5	0.17	0.44
1955	38.8	0.63	1.62
1955 (known)	38.8	0.12	0.31
1956 (known)	38.8	0.23	0.59
1956	38.8	0.41	1.06
Average	38.7	0.31	0.80