of disodium 2-sulfoethyl α-sulfostearate with sodium 9,10-dichlorooctadecyl sulfate. The syndet-syndet formulations give perfectly clear solutions in hard water.

Soap-Syndet Formulations

Soap in the form of sodium oleate or a tallow soap could be used as the only active ingredient in the general formulation but opaque, milky dispersions resulted when used in washing experiments in hard water. Other effects are shown in Table I. All systems listed were stable for 90 days or more.

The pH of the soap-syndet systems ranged from 9.3–10.5; viscosity was decreased by the presence of synthetic detergent. Soap can be used with esters of α-sulfo acids or with soluble forms of the tallow alcohol sulfates. Formulations with the isethionate ester or the *N*-methyl tauride of oleic acid in place of the α-sulfo esters (formations No. 8 and 10) gave slightly lower values for detergency in hard water ($\Delta R = 12$, 15, respectively). Combinations of sodium oleate with a sulfated nonionic (No. 8) gave the best foaming properties in hard water. Combinations in which sodium 9,10-dichlorooctadecyl sulfate was one of the active ingredients (No. 7, No. 12) had superior detergency in hard water.

ACKNOWLEDGMENT

Assistance in the preparation and properties of liquid detergent formulations by M. V. Nunez-Ponzoa.

REFERENCES

1. Anonymous. Soap Chem. Specialties *32*, No. 3, 19 (1956); *34*, No. 3, 207–208 (1958); *36*, No. 3, 183 (1960); *37*, No. 3, 181–182 (1961); *38*, No. 3, 159–160 (1962).
2. Anonymous. Chem. Eng. News *40*, No. 37, 33–34 (1962).
3. Draves, C. Z., and O. L. Sherburne, Am. Dyestuff Reptr. *39*, 771–772 (1950).
4. Knaggs, E. A. Paper presented before the Minneapolis meeting of the American Oil Chemists' Society, October 1963.
5. McCutcheon, J. W., Soap Chem. Specialties *33*, No. 8, 43–46, 111, 113 (1957).
6. Ross, J., and G. D. Miles, Oil & Soap *18*, 99–102 (1941); ASTM Method D-1173-53.
7. Stirton, A. J., JAOCS *39*, 490–496 (1962).
8. Tillotson, C. C., Soap Chem. Specialties *35*, No. 2, 49–52, 169 (1959).
9. Weil, J. K., and A. J. Stirton, JAOCS *41*, 355–358 (1964).
10. Weil, J. K., A. J. Stirton, R. G. Bistline, Jr. and E. W. Maurer, JAOCS *36*, 241–244 (1959).

[Received March 13, 1964—Accepted June 12, 1964]

Continuous Refining of Crude Cottonseed Miscella

L. S. CRAUER, The De Laval Separator Company, Poughkeepsie, New York, and H. PENNINGTON,
S. A. Camp Cotton Oil Company, Schafter, California

Abstract

A simple, easily controlled process for continuous caustic refining of crude cottonseed miscella in a two-stage system is described. The effect of crude oil quality, oil:hexane ratios, temp, mixing conditions and chemical treatment are noted. The chemical reactions in the process are followed microscopically. The process yields a refined oil of less than: 1.0 bleach oil color, 0.03% free fatty acid and 15 ppm soap, and with 30–40% oil savings over Official Cup Loss. The by-product soap may be used advantageously in the meal from the extractor unit.

Introduction

ALTHOUGH A NUMBER of basic patents (1) for the refining of crude oils in the miscella state have issued in the past two decades, the acceptance of this refining technique as a general practice has been slow due to delay in the development of appropriate equipment and marketing practices. The recent trend toward complete processing of raw materials to finished products at the source area has stimulated an interest in miscella refining of crude solvent extracted and prepressed solvent extracted oils at the seed mill. Thus, the continuous refining of the crude oil-hexane mixture in a completely closed system is a natural development.

The chemical and physical properties of the crude miscella differ considerably from conventional hydraulic, expeller or solvent extracted crudes. The fact that this miscella crude oil may be treated continuously in a relatively simple system to yield quality products makes the De Laval Miscella Refining System a unique process.

This miscella refinery process is shown in Figure 1.

Description of Process

In this process, the crude miscella source may be a) from the pre-evaporator of a direct-solvent extraction plant, b) from a blend of prepressed crude oil and solvent extracted miscella from the press cake, or c) possibly a reconstituted blend of crude oil with hexane.

The crude oil-hexane mixture, 45–65% oil: 35–55% hexane, is pumped through either a heater or cooler to bring to the desired processing temp range, then to a motorized Cuno or similar filter to remove any meal, scale or insoluble impurities that may be present from the extractor, pre-evaporator or storage tank.

The feed next passes through a flow measuring device, such as an indicating rotameter with ratio controller for the reagent treatment system, and enters the pretreatment additive and mixing section. Here a small dosage pump meters an additive in ppm quantities.

The pretreated crude miscella then enters the reaction section, where the refining agent is intimately intermixed and contacted for a given period of time until the impurities in the crude oil are precipitated in the soap phase.

This reaction mixture passes to a heater to assure proper temp for centrifugation in the Hermetic (2) Miscella Separator.

In this specially designed centrifuge, the light colored refined miscella is readily separated from the dark, gummy, fluid soapstock.

The light yellow miscella is pumped to the stripper of the solvent extraction plant for recovery of the hexane. Leaving the stripper at 220F, the refined oil passes to a pressure leaf-type filter, with dosage and precoat system for removal of last traces of soap and any extraneous impurities, before cooling and entering storage as a quality refined or bleached oil product.

The soapstock from the centrifuge may be pumped: to desolventizer-toaster as a meal additive; to a continuous acidulation system for acid oil recovery; or to storage.

Chemistry of Process

Laboratory and actual plant experience have shown that, with direct solvent extracted crude cottonseed oils, the processing conditions in the refinery will

---

[1] Presented at the AOCS Meeting in Minneapolis, 1963.

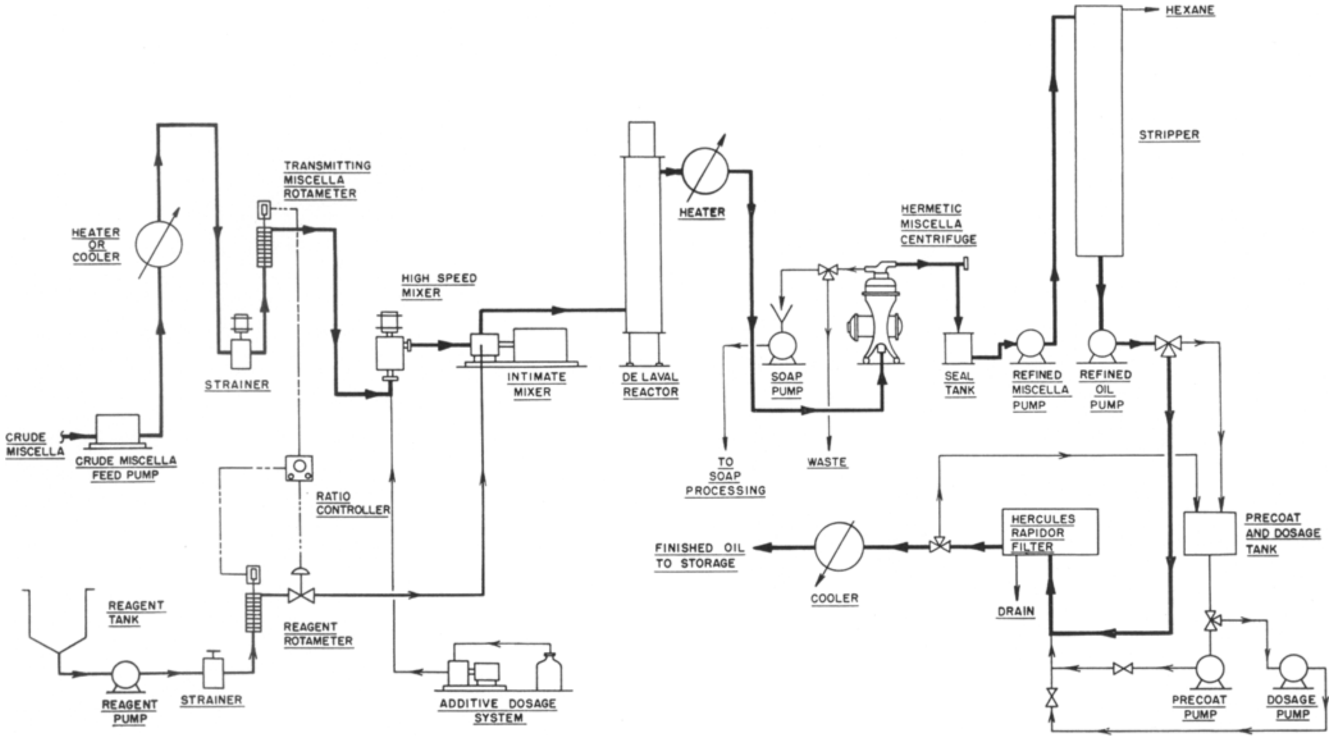

FIG. 1. Schematic flow diagram for DeLaval miscella refinery.

vary dependent upon preprocessing treatment in the extractor.

The amount of moisture addition to the dehulled, delinted seed, the temp in the cooker, the hold time in the cooker, as well as conditioning at the flaking roll, are all important to quality of the meal. These factors, likewise, influence the extraction and crude miscella oil. With the deep bed extractor, in direct solvent extraction of California Acala cottonseed, a portion of the gossypol is extracted into the crude miscella. This produces an extracted flake of as low as 0.5–0.8% total gossypol and ca. 0.1% free gossypol content.

Typical analyses for crude solvent extracted oils from this same source for two growing seasons are as follows:

> % Free fatty acid—0.6–1.5; % Phosphatides—1.0–2.0; % Total gossypol—0.4–1.1, Theoretical loss—2.5–3.7; AOCS Official Cup Loss—5.3–6.7; Official Refined Oil Color—3.0–6.3 Red and Official Bleached Oil Color—0.5–2.2 Red.

This crude miscella can be refined in the range of 45–65% oil: 35–55% hexane ratio. When the oil is blended with the hexane in these ratios, there is a definite advantage in pumping, heating, mixing and centrifuging through the reduction in viscosity and specific gravity. Crude cottonseed oil at 80F has a viscosity of 254ssu (55 centipoise), and a sp gr of 0.92. A 60% oil: 40% hexane mixture at 80F has a viscosity of only 47ssu (10 centipoise), and 0.76 sp gr.

In the pre-evaporator, the direct solvent extracted miscella can be held at the desired oil:hexane ratio by an automatic temp controller unit to within ±1%.

The advantage of miscella refining is in the immediate treatment of the crude oil-hexane mixture, soon after the oil has been extracted from the flakes, and before stripping of the solvent has set the color. To maintain this advantage, it is important to refine fresh crude oil miscella, preferably in the first two hr, and to minimize storage time. However, with this described process treated miscella has been successfully refined after as much as 24 hr delay.

The crude miscella refines readily when pretreated with a small percentage of an additive. Inorganic acids, such as sulfuric and phosphoric and organic acids in carboxylic classification, such as glacial acetic, citric and tartaric, as well as hydrogen peroxide, are

FIG. 2. Soap micelles suspended in oil hexane phase.

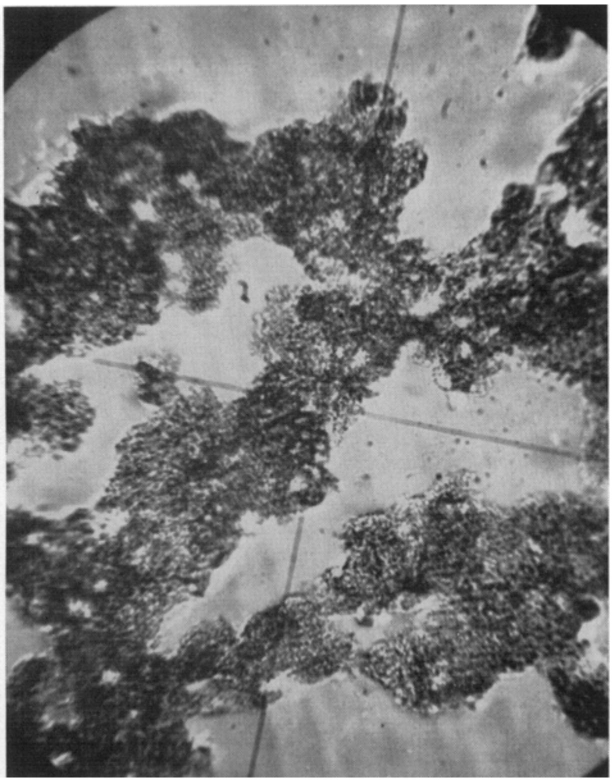

FIG. 3. Agglomerated soap in oil hexane phase.

a few that have been found effective. Those agents meeting the requirements of the approved list of the Federal Pure Food and Drug Administration are used in continuous refining. The final choice of agent is generally dictated by patent limitations, availability and cost. The additive is effective in as low as 50 ppm dosage by wt of miscella flow, and may be added at any point in the system prior to the alkali treatment; i.e., in the full miscella flow, at the pre-evaporator, or at an in-line mixer following the feed pump. The additive enters into immediate reaction with the crude miscella. Most effective dosage range to the crude miscella for glacial acetic acid has been 100–1000 ppm, with 100–400 ppm generally used. The increase in acidity on a crude oil basis with this dosage is in range of 0.05–0.2%, titrated as oleic acid. This preliminary treatment prior to refining, has been found necessary to yield a light colored refined oil product in a continuous system with only minutes of hold time capacity.

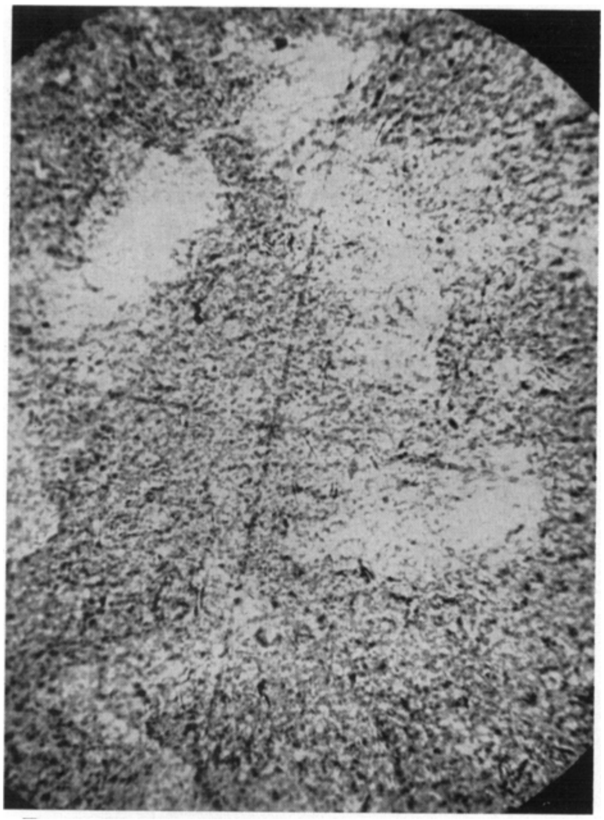

FIG. 4. Phosphatidic crystals absorbed on soap mass.

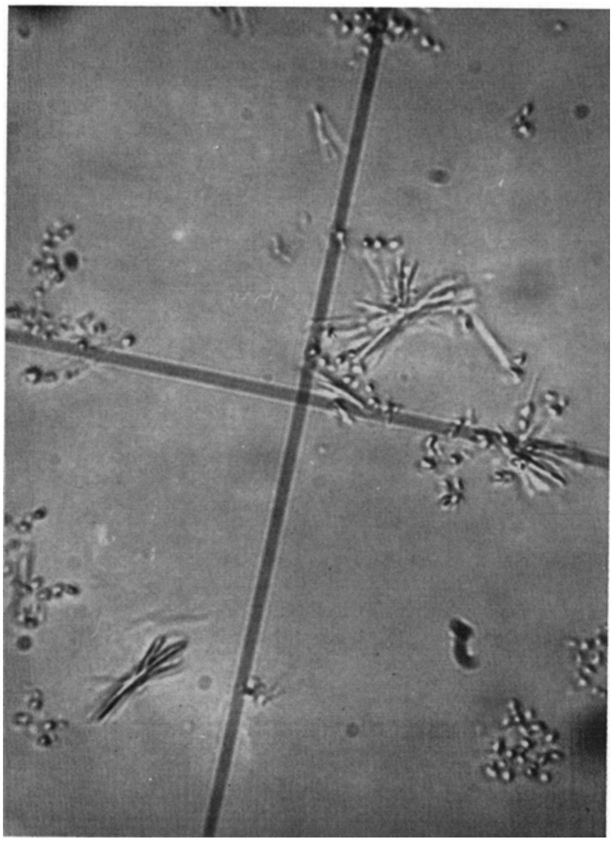

FIG. 5. Phosphatidic crystals at ca. 1000 magnification.

The acid dosage has a definite effect on finished oil quality. With all other processing conditions remaining the same, an increase of acid pretreatment improves the refined and bleached oil color.

The pretreated crude miscella is alkali refined with usually 10–16° Bé caustic at 0.25–0.45% excess treat over the theoretical requirement to neutralize the free fatty acid. The treat is calculated on the crude oil basis of throughput flow.

A study of the chemical reaction between the caustic and crude cottonseed oil miscella has shown that the reaction progresses much more rapidly at 120–140F than at 80–100F, with no deleterious effect on the finished oil product. Direct solvent extracted crude cottonseed oil miscella can be refined in a matter of a few minutes at 120–135F.

In the alkali reaction section of the miscella refinery, the functional design of the mixing equipment has been found to be an important factor. The reagent and crude miscella feed are first intimately dispersed in a multiple shear mixer of the rotary type, followed by specially designed De Laval contact mixers.

The progress of the chemical reaction through the alkali refining section can be followed very closely by microscopic examination.

TABLE I

Data on Refined Oil Quality and Loss in Miscella Refining of Crude Cottonseed Oil

Crude solvent extracted cotton oil analyses						Caustic refining of the crude cotton oil miscella				
Run No.	% FFA	Theoretical loss	Official cup results			Ratio oil:hexane	Plant loss	Finished oil		
			Loss	R.O. color	B.O. color			% FFA	R.O. color	B.O. color
1	1.0	3.3	5.8	6.3	2.1	65:35	4.0	0.03	4.4	0.7
2	1.4	3.7	6.7	4.7	2.2	49:51	4.2	0.02	5.0	0.8

In Run No. 1, the % oil savings over cup loss is 31%, whereas in Run No. 2, the % oil savings over cup loss is 37%.

As soon as the reaction mixture leaves the intimate mixer, the reaction between the free fatty acids and caustic is complete and has produced soap micelle. See Figure 2.

These soap micelles appear rust brown in color, granular and have a sponge-like appearance microscopically. The oil-hexane phase leaving this mixing stage is purple.

As seen in Figure 3, the soap micelles have a definite affinity for one another and quickly agglomerate to form large and dense clusters with little oil occlusion. These photographs represent reaction changes within an interval of a few seconds.

In the contractor mixer section, following the intimate dispersion, the reaction between the reagent-soap phase and oil-hexane phase continues. The phospho-lipides and color bodies are precipitated here as a crystal fraction on the soap micelle or adsorbed by them. The progressive reaction of the gossypol fraction in the crude cottonseed oil may be followed, as it passes through all the color changes, for reaction products to complete removal. The oil fraction will change progessively from red to red browns, to red-orange, then orange and finally a light yellow.

Figure 4 shows this adsorption of the phosphatidic phase on the soap mass. In polarized light, the phosphatides appear as blue, rod-like crystals against the background of the soap mass. These crystals are only 8–12 μ in length by 1–2 μ in width.

On Figure 5, taken at higher magnification, the phosphatidic crystals appear in better detail. The tendency of these crystals to clump together is evident.

In the reaction section, the hold time is influenced by the acid pretreatment, the alkali treat and the desired quality of finished oil product. Through an extensive research program confirmed by field tests, ideal conditions have been readily established which result in reduction of Lovibond Colors of the refined oil from 35/7.5 in a 1 in. tube to 35/3.9 in a 5¼ in. tube.

Phosphatidic content of the crude miscella has a definite influence in the design of the mixing section of the plant.

With variation in the oil:hexane ratio, there is a definite change in mixing requirement.

Following completion of the reaction in the mixing section, the mixture flows through a heater to maintain or elevate temp for centrifugation. Above 138F, there is volatilization of the hexane.

The heart of this miscella refining process is the Hermetic miscella separator. This unit has been well described in a paper by R. E. Thrush (3). To meet the requirements of specific gravity differential between the oil-hexane and soapstock phases and eliminate any possibility of solvent loss, the Hermetic miscella separator was developed. The discharge diameter of the soapstock phase is larger than that of conventional type Hermetic centrifuge, and double seals with water barrier are provided at the inlet to the spindle.

As an integral part of a completely closed system, the Hermetic centrifuge operates under pressures of 55–120 psi at the feed inlet, and 45–90 psi at the miscella discharge. The pressure differential required is dependent principally upon Baumé of caustic used as refining agent, the oil:hexane ratio in miscella, and any extraneous accumulation of insoluble impurities in the bowl.

In this centrifuge, the light brown to black, rather gelatinous, free flowing soapstock is separated from the light yellow refined miscella. The soapstock has a lower viscosity than generally observed in conventional cottonseed oil refining, and contains from less than 1–3% hexane. Even when discharged into an open hopper to be pumped away to further processing, the odor of hexane in the soapstock is barely discernible.

The refined miscella discharging from the centrifuge will contain less than 0.05% free fatty acid, has a refined oil color of 3.6–8.3 and contains 15–150 ppm soap (4) on an oil basis. Usual value is in range of 10–50 ppm soap, thus eliminating the need for water-washing.

From the centrifuge, the refined miscella passes directly to the evaporation and stripping section of the solvent plant for recovery of the hexane. The refined oil, leaving the stripper, is pumped to a pressure-leaf filter where the final polishing of the refined oil is accomplished. This filter removes the small quantities of soap, pipe scale and any other impurities present. Finished oil contains less than 15 ppm soap.

In Table I is a tabulation of the plant refining loss and finished oil quality experienced in the Continuous Miscella Refinery that has been in operation on direct solvent extracted crude miscella for more than a year at the S. A. Camp Cotton Oil Co. near Shafter, Calif.

This data shows that the miscella refinery may be so operated as to yield 30–37% oil savings over offical cup loss on the direct solvent extracted crude miscella. As the ratio of oil to hexane increases in the miscella, the amt of neutral oil entrainment also will increase. The refined oil and bleached oil color of the finished oil equals or exceeds the official cup figures. More recent tests on off grade oils indicate that this system will approach 40% or more savings over official cup loss.

In direct solvent extraction plants, it has been found advantageous to pump the soapstock from Hermetic centrifuge discharge directly to the desolventizer-toaster. By adding the soapstock to the meal, there is an increase in oil content, a gain in meal wt, an increase in protein solubility and a decrease in free gossypol content. The meal so treated is easier to handle, and also may be readily pelletized.

ACKNOWLEDGMENT

Photomicrographs by T. F. Wacker and C. K. Conklin.

REFERENCES

1. Thurman, B. H., U.S. 2,260,731 (1941); Mattikow, M., U.S. 2,576,957 (1951) and Cavanagh, G. C., U.S. 2,789,120 (1957).
2. "Hermetic" is a registered trademark.
3. Thrush, R. E., The Oil Mill Gazetter *66*(2), 11–13, 30–31 (1963).
4. Checked by AOCS Tentative Method Cc15-60 and by Sodium Analyses using Magnesium-Uranyl-Acetate.

[Received October 9, 1963—Accepted May 7, 1964]