

addition, not all soils would be expected to give rise to the same interfacial properties as Graphon. However, this study has shown that very low concentrations (a few ppm) of calcium ions can have marked effects on the packing of surfactant molecules at the graphite/surfactant solution interface and, moreover, on the attachment of graphite particles to cotton.

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REFERENCES

- 1a. Zettlemoyer, A. C., G. J. Young, and J. J. Chessick, *J. Phys. Chem.* **59**, 962 (1955).
- 1b. Chessick, J. J., F. H. Healey, and A. C. Zettlemoyer, *Ibid.*, **60**, 1345 (1956).
- 1c. Chessick, J. J., and A. C. Zettlemoyer, "Advances in Catalysis," Vol. XI, pp. 263-299, Academic Press (1959).
2. Skewis, J. D., and A. C. Zettlemoyer, IIIrd International Congress of Surface Activity, Vol. II, Sec. B/III/1, 401, Cologne (1960).
- 3a. Zettlemoyer, A. C., and J. D. Skewis, Paper presented at the meeting of the American Chemical Society, September 1959 (in press).
- 3b. Skewis, J. D., Ph.D. Thesis: "The Adsorption of Surfactant Anions and Gegenions to the Graphon/Aqueous Solution Interface," Lehigh University, 1959.

- 4a. Ginn, M. E., and J. C. Harris, *J. Phys. Chem.*, **62**, 1554 (1958).
- 4b. Botre, C., V. L. Crescenzi, and A. Mele, *Ibid.*, **63**, 650 (1959).
- 4c. Williams, R. J., J. N. Phillips, and K. J. Mysels, *Trans. Far. Soc.*, **51**, 728 (1955).
5. van Voorst Vader, F., IIIrd International Congress of Surface Activity, Vol. II, Sec. B/II/1, 276, Cologne (1960).
6. v.d. Tempel, M., *Rec. trav. chim.*, **72**, 419 (1953).
7. Stüpel, H., "Synthetische Wasch- und Reinigungsmittel," p. 125, Stuttgart 1954.
- 8a. Jayson, G. G., *J. Applied Chem.*, **9**, 422 (1959).
- 8b. Porter, A. S., IInd Congress on Surface Activity, I, p. 477, London, 1957.
9. Vitale, P. T., *JAOCS*, **31**, 341 (1954).
10. King, A., *Trans. Far. Soc.*, **37**, 168 (1941).
11. Schwarz, W. J., A. R. Martin, and R. G. Davis, Paper presented at the meeting of the American Chemical Society, Division of Cellulose, Wood and Fiber Chemistry, Chicago, September 1961.
12. Niven, W. W., Jr., "Industrial Detergency," Reinhold Publishing Corp., New York, N.Y., 1955, p. 5.
13. Reich, I., Ph.D. Dissertation, University of Southern California, Berkeley, Calif., 1955.
14. Schwartz, A. M., J. W. Perry, and J. Berch, "Surface Active Agents and Detergents," Vol II, Interscience Publishers Inc., New York, N.Y., 1958, p. 489.
15. Goette, E. K., *J. Colloid Sci.*, **4**, 459 (1949).
16. Vitale, P. T., J. Ross, and A. M. Schwartz, *Soap and Chem. Specialties* **32**, 41 (1956).
- 17a. Ross, J., P. T. Vitale, and A. M. Schwartz, *JAOCS*, **32**, 200 (1955).
- 17b. Vitale, P. T., *Ibid.*, **31**, 431 (1954).
- 18a. Compton, J., and W. J. Hart, *Ind. Eng. Chem.*, **45**, 597 (1953).
- 18b. Compton, J., and W. J. Hart, *Ibid.*, **43**, 1564 (1951).
- 18c. Hart, W. J., and J. Compton, *Ibid.*, **44**, 1135 (1952).
19. Durham, K., *J. Applied Chem.*, **6**, 153, (1956).

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Refining Crude Cottonseed Oil Dissolved in Hexane¹

M. A. ZEITOUN,² W. B. HARRIS, and W. D. HARRIS, Cottonseed Products Research Laboratory, Agricultural and Mechanical College of Texas, College Station, Texas

Abstract

Measurements were made of the surface tensions of mixtures of cottonseed oil and hexane and of their interfacial tensions against water and caustic soda solutions. Attempts were made to study the reaction rate between the two phases. The results show that in caustic refining of hexane miscellas the caustic is readily dispersed into the oil-hexane phase.

Refining losses were found to be lower for miscellas containing less than 70% oil. Concentrations as low as 40% were refined successfully. The losses were inversely related to the viscosity of the solution.

Introduction

IT IS KNOWN that the red color of solvent-extracted cottonseed oil is made more difficult to remove by the heating necessary to evaporate the solvent (1). For this reason the refining of oil dissolved in hexane is of interest to persons operating solvent extraction plants. Literature references indicate, however, that color removal during miscella refining is a major problem. Very little information is given about optimum conditions for refining oil-hexane miscellas.

Mattikow (2) states that decolorizing the oil is not successful when the oil content is less than 77%. Folzenlogen (3) claims that color can be removed from 40% oil miscellas if polypropylene glycol is added as a surface active agent. James (4) indicates that 50% miscella concentration is most effective for neutralization and decoloration. Thurman (5) reports that in a two-step process, 75% miscella refines to a good color and that 50% is almost as

good, providing a surface active agent such as polypropylene glycol is used. A recent patent (6) has been issued covering the use of polypropylene glycol in miscella refining. Cavanagh (7) refines 40% miscella successfully, providing the meats are treated with soda ash prior to removal of the oil. He indicates that even 19% miscella can be refined to a low bleach color, but he does not give the refined color nor the amount of bleaching earth used. Frankel (8) describes a two-step refining process in which 25% miscella yields superior results.

According to James (4), considerable difficulty is encountered in obtaining effective contact between caustic solutions and miscella. Sufficient contact for neutralization of the fatty acids is said to be easy, but the coagulation of phosphatides and the removal of color are said to require better mixing. He indicates that successful mixing can be obtained using surface active agents or mechanical homogenizers.

Some of the physical properties which would affect mixing of caustic solutions and miscella are interfacial and surface tensions, viscosity, and density. No data were found in the literature for interfacial and surface tensions. The viscosities and densities of oil-hexane solutions have been published (9,10,11). These references point out that the reduced viscosity and gravity of miscella solutions make the separation of soapstocks easier. However, no correlations between refining losses and viscosity or density were found.

In this investigation, surface and interfacial tensions were measured for miscella-caustic soda and miscella-water systems. The refining of crude cottonseed oil dissolved in hexane was studied. The variables were the amount of hexane present, the quantity of caustic used, and the concentration of the caustic.

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² Present address: Cairo, Egypt.

Experimental Procedures

Raw Materials. In this discussion the word "miscella" will be used to indicate an oil-hexane mixture obtained during solvent extraction of the oil. The miscella was obtained from a batch type extractor explained by Wamble (12). Part of the miscella was completely freed of hexane to obtain a sample for FFA and cup refining loss determinations. The rest of the miscella was evaporated under a vacuum of 10 to 14 inch of mercury and at a temperature not exceeding 40C. Under these conditions, a miscella of 77.5% oil was obtained. Lower concentrations were prepared by diluting this material with hexane. The cup loss analysis for the desolventized oil is given in Table I.

TABLE I
Cup-Loss Analysis of Solvent Extracted Cottonseed Oil

% Free fatty acids.....	2.8%
Lye: 16°Bé.....	8.9 g/100 g oil
Refining loss.....	7.6%
Refined color.....	3.0%
Soapstock.....	dark and fine

The cottonseed oil used for rate, surface tension, and interfacial tension studies was refined, bleached, and then washed twice with water to free it from traces of soap. The FFA content was less than 0.01%.

Surface and Interfacial Tension Measurements. A Cenco-du Nouy tensiometer was used for the measurement of surface and interfacial tensions. The calibration was checked frequently by comparing measurements for distilled water and benzene with values reported in the literature.

Density and Viscosity Measurements. These values (11) were obtained with a pycnometer and Ostwald viscometer. When compared with data from reference (11), experimental values for viscosity were slightly lower for dilute solutions, probably due to variation in the oils used. No other significant deviations were noticed.

Reaction Rate Studies. Attempts were made to study the rate of the reaction between *c/s* oil-hexane solutions containing free oleic acid and caustic soda solutions. The principle of a wetted wall column was first tried, but neither solution wetted the wall of the glass column in the presence of the other. Next a falling drop method frequently used in the study of liquid-liquid extraction systems was tried. A glass tube 2 inch in diam and 5 ft high was fitted with a nozzle at the top and a means of collecting the dispersed phase drops at the bottom. The tube was filled with refined *c/s* oil (continuous phase), and the formation of caustic soda droplets falling through the oil was studied. It was found that when even a small amount (0.1%) of free oleic acid was present, soap formed at the interface and reduced the surface tension to the point that drops would not form. The caustic descended in a thin stream. Mixing the oil with hexane resulted in dispersal of the caustic stream into very small droplets, forming a cloudy haze in the tube. The study was not carried further.

Refining Method. The mixtures to be refined were placed in 250-ml centrifuge bottles, the required amount of caustic solution was added, and the contents were agitated by T-shaped paddles attached to the drive mechanism of a standard A.O.C.S. refining apparatus. (A mechanical shaker was unsuccessful as the soapstock would not separate.) The temperature was controlled at 25C for 30 min with agitation at 250 rpm. The temperature was then raised to 50C, and stirring reduced to 70 rpm. In 10 min the

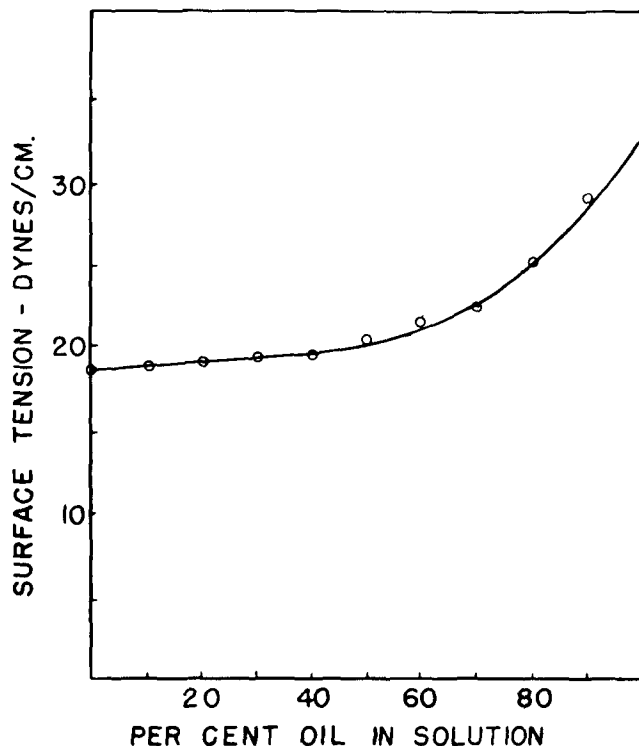


FIG. 1. Surface tensions of cottonseed oil-hexane solutions.

paddles were removed, returning as much as possible of the sample which clung to the paddles. The bottle was stoppered and centrifuged for 10 min at 2,000 rpm in a Universal Centrifuge. The refined sample was then decanted. Oil and soapstock weights were obtained.

Refining loss results were reproducible within 2%.

Hexane was removed from the refined sample by vacuum and a little heat. The refined color of the oil, free of solvent, was determined photometrically.

Experimental Results

Surface Tensions. The surface tensions for *c/s* oil-hexane solutions are given in Figure 1. The oil concentration has little effect until it reaches 50%. From 50% to 100% the surface tension increases from 20.6 dynes per cm to 32.4.

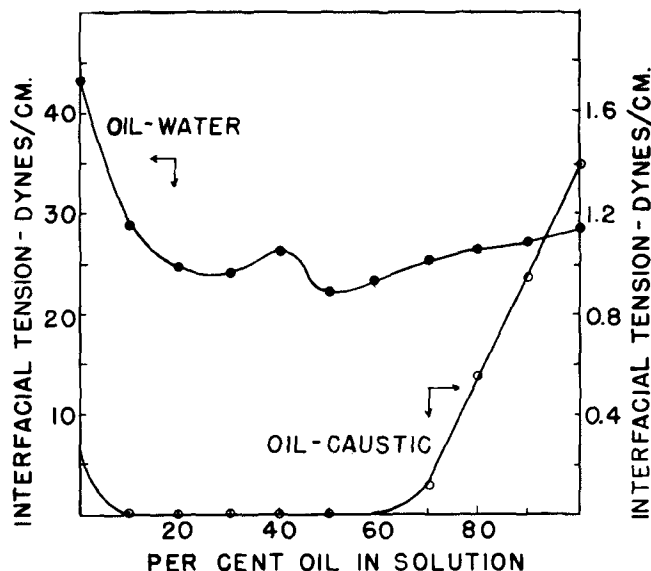


FIG. 2. Interfacial tensions of cottonseed oil-hexane solutions against water and 12°Bé caustic.

The surface tension of hexane-free oil did not change when the FFA content was varied from .01% to 3.39%.

Interfacial Tensions between *c/s* oil-hexane solutions and a water or caustic soda phase are given in Figure 2. The concentration of the caustic had no effect within the range studied, 12°Bé to 22°Bé.

The values for *c/s* oil-hexane solutions against caustic are very low at any concentration, and they are practically zero in the 10% to 50% range.

Against a water phase, the values are much higher. Hexane has a higher value than pure oil, 43.4 vs. 28.5 dynes per cm. A minimum value of 22.2 was found at 50% oil concentration. The value at the 40% level was checked several times. The hump in the curve at this point cannot be explained.

The values for interfacial tension given in Figure 2 were approximately halved when the FFA content was raised from .01% to 3.39%.

Refining Tests

Refining Losses. Figure 3 shows refining loss and color obtained on miscellas of different hexane content. The miscellas were refined with 3.3 g of 24°Bé caustic per 100 g of oil.

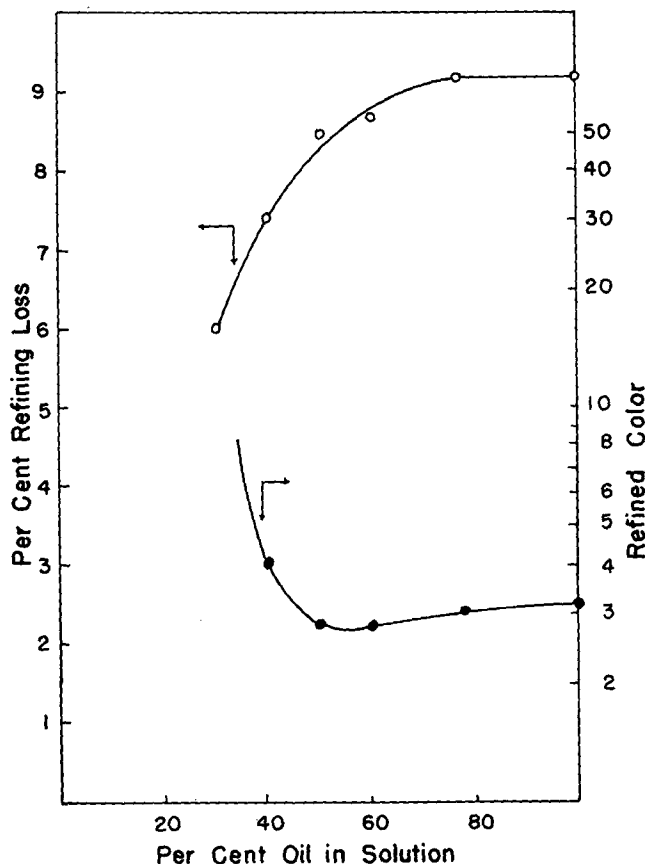


FIG. 3. Refining of cottonseed oil-hexane miscellas with 24°Bé caustic.

Miscellas containing as little as 40% oil can be refined to a good color with a considerable gain in yield of refined oil. Fifty or 60% gives a better color although refining losses are higher. There was little reduction in R.L. when the oil content was above 70%.

Caustic Concentration. Miscella (77.5%) was treated with various concentrations of caustic soda containing the same quantity of NaOH as above. The effects of caustic concentration on R.L. and color are shown in Figure 4. The best refined colors were

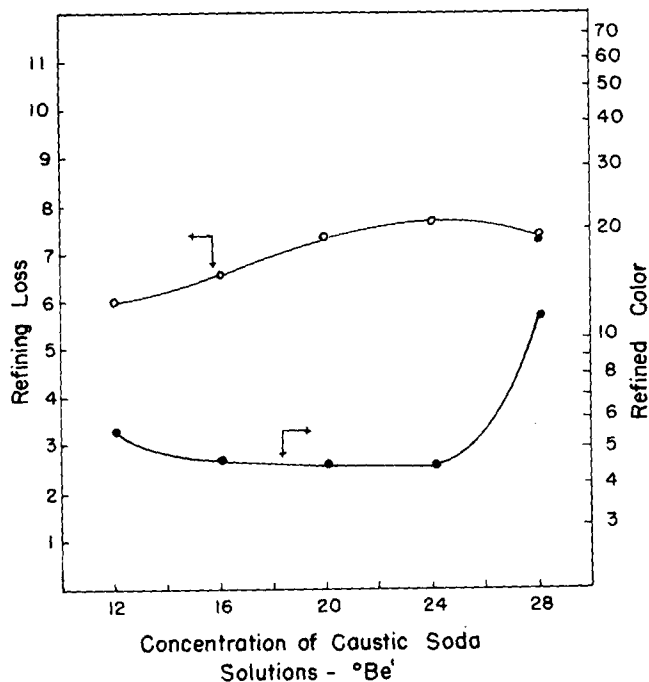


FIG. 4. Refining of cottonseed oil-hexane miscella with different concentrations of caustic.

obtained using 24°Bé caustic. Although this corresponded to the maximum R.L., the improvement in color was so definite that 24°Bé would be favored for refining.

Quantity of Caustic. Figure 5 shows the results of refining the 77.5% miscella with different quantities of 24°Bé caustic. Increasing the quantity meant a considerably increased R.L. The color of the oil was not much affected when the quantity changed from 3.3 to 5 g per 100 g of oil.

Discussion of Results

The interfacial tension of *c/s* oil against caustic soda solution is very low. It is lowered practically

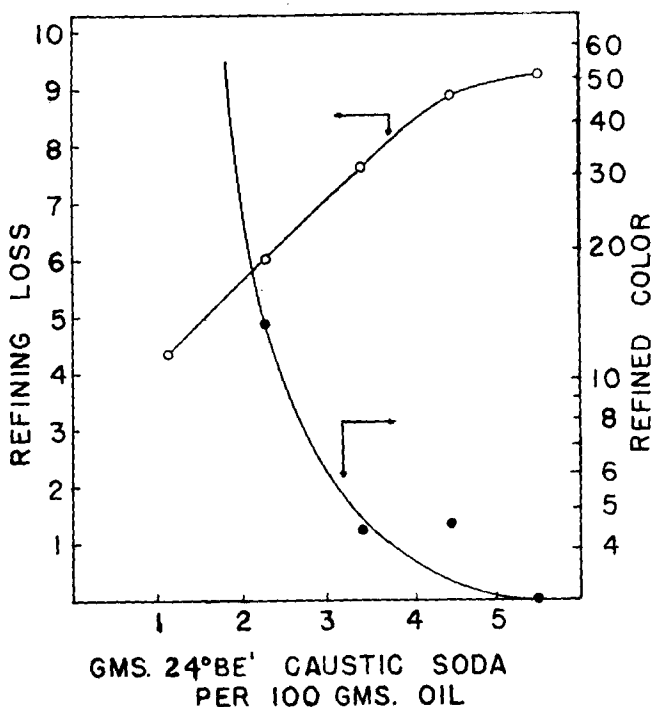


FIG. 5. Refining of 77.5% cottonseed oil-hexane miscella with different quantities of 24°Bé caustic soda.

to zero by the addition of hexane or the presence of fatty acids. Attempts to study the reaction rate of caustic droplets falling through *c/s* oil and oil-hexane solutions failed because the interfacial tensions were so low that the droplets broke and dispersed into the oil phase, giving a cloudy or hazy appearance.

It appears that caustic solutions are readily dispersible in *c/s* oil and oil-hexane solutions. Mixing of the phases should present no problem.

It has been reported that the low density and viscosity of oil-hexane miscellas result in a higher settling rate of the soap (5,7). The increase in settling rate is said to reduce the R.L. because less material is entrained in the soap. A study of this relationship was made by plotting the R.L. vs. the difference in density between soapstock and solution, and by plotting the R.L. vs. the reciprocal of the viscosity of the solution. (According to Stoke's law, the settling rate, and presumably the refining loss, varies directly with differences in density and inversely with viscosity.)

The density plot was irregular, and there was no apparent correlation. On the other hand, the viscosity plot, Figure 6, showed R.L. to be closely related to viscosity. Since the density had no effect, and also because the settling time was very short due to use of a centrifuge, it is believed that the effect of viscosity upon R.L. was not due to the enhanced soapstock settling rate although no other explanation presents itself. It is worth noting that the reciprocal of the viscosity does not change very rapidly above 70% oil concentration. This explains why miscella R.L. was not substantially improved until the concentration dropped below 70%.

The absolute values of the R.L. depend largely on whether a continuous or batch type of process is used, and upon the means of separation. The values reported do not necessarily reflect the results which would be obtained commercially. The refined colors are not affected so much by process conditions, and they are believed to be representative of colors which would be encountered commercially.

Two important observations are that R.L. is not considerably reduced until the oil concentration is less than 70% and that low refined colors can be obtained with miscella having an oil concentration down to 40%.

The quantity of caustic soda solution used has a great effect on the R.L. The refined color is not much affected unless insufficient caustic is used to complete the refining.

These results show that miscella refining does not necessarily introduce a color problem. In this study there were several factors which may have helped the refined oil color. The oil was produced from one lot of seed grown in Central Texas. It was extracted in a batch extractor that may have extracted fewer color bodies. The miscella was relatively fresh. Last, and most important, the miscella was concentrated under vacuum without complete removal of solvent so that color setting due to high temperatures was avoided.

Summary and Conclusions

1. Surface tensions of *c/s* oil-hexane solutions and their interfacial tensions against water and caustic soda solutions were measured. Hexane and FFA were

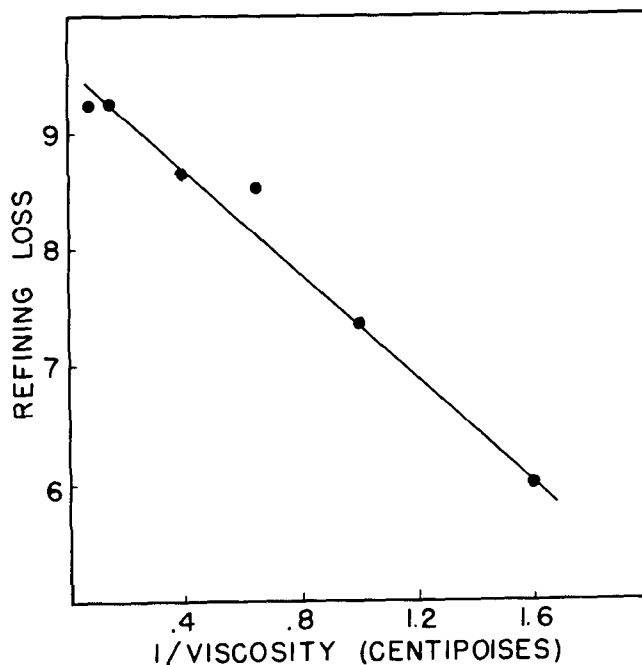


Fig. 6. Refining loss as an inverse function of viscosity.

found to lower the interfacial tensions against caustic solutions.

2. The formation of caustic soda droplets in *c/s* oil-hexane solutions was studied. The presence of FFA as low as 0.1% broke the droplets to a thin stream. Hexane also broke the droplets to small size. This result, backed by the interfacial tension measurements, indicated that in caustic refining the caustic is readily dispersed into the oil, thus facilitating the reaction rate.

3. Although it has not been definitely shown that the mixing of *c/s* oil with hexane slows down the rate of saponification, it has been demonstrated that the presence of hexane allows the use of higher concentrations of caustic solutions with less danger of saponifying the neutral oil.

4. Viscosities and densities of *c/s* oil-hexane solutions were measured. Correlating these to the R.L. of the oil-hexane miscellas showed that lower viscosity is a more important factor than lower density in reducing the R.L.

5. It was found that R.L. is substantially reduced for miscellas containing less than 70% oil. Concentrations as low as 40% oil were refined successfully with a considerable gain in the refined oil yield.

REFERENCES

1. Vix, Pollard, Spadero, and Gastrock, *Ind. Eng. Chem.*, **38**, 635 (1946).
2. Mattikow, M., U. S. Pat. 2,576,957 (1951).
3. Folzenlogen, R. G., U. S. Pat. 2,563,327 (1951).
4. James, E. H., *JAOCS*, **35**, 76 (1958).
5. Thurman, B. H., *Ibid.*, **30**, 493 (1953).
6. Schmitt, U. S. Pat. 2,878,275 (1959).
7. Cavanagh, G. C., *JAOCS*, **33**, 528 (1956).
8. Frankel, E. E., *Chem. Eng.*, 356 (1953).
9. Decossas, K. M., F. A. Deckbar, and J. L. Hecker, U. S. Dept. of Agr., Agr. Res. Adm., Bureau of Agr. and Ind. Chem., A.I.C. -304 (1951).
10. Decossas, K. M., *et al.*, *Ibid.*, A.I.C. -292 (1950).
11. Magne, F. C., and E. L. Skau, *Ind. Eng. Chem.*, **37**, 1097 (1945).
12. "Description of Bench Scale Solvent Extraction Process for Cottonseed," mimeograph, Texas Engineering Experiment Station, 1960.
13. Zeitoun, M. A., "Studies of the Refining of Crude Cottonseed Oil and Its Solutions in Commercial Hexane," Dissertation submitted to the Agricultural and Mechanical College of Texas, May, 1958.

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