

miso. The new method (5) makes an improved quality of miso in a shorter fermentation period than the old method by using dehulled soybean grits which absorb water and which cook rapidly and uniformly. If the new method of making miso is adopted, the problems of water absorption and cooking will be eliminated in the miso process.

Acknowledgment

This work is part of a program at the Northern Regional Research Laboratory on the use of U.S. soybeans in foreign markets. The study on water absorption of soybeans was undertaken in part as a result of a special survey made in Japan by one of us (A.K. Smith) (6) and subsequent joint studies (4,5,7, and

other proposed publications) at the Northern Laboratory sponsored by the American Soybean Association, Hudson, Ia., and the Foreign Agricultural Service and Agricultural Research Service of the U.S. Department of Agriculture. The samples of Japanese beans were supplied by the Japanese-American Soybean Institute.

REFERENCES

1. Beckel, A.C., and Cartter, J.L., *Cereal Chem.*, **20**, 362-368 (1943).
2. Brown, O.A., Stone, R.B., Jr., and Andrews, Henry, *Agr. Eng.*, **38**, 666-669 (1957).
3. Personal communication.
4. Shibasaki, K., and Hesselstine, C.W., *Bact. Proceedings*, 49-50 (1960).
5. Shibasaki, K., and Hesselstine, C.W., "Developments in Industrial Microbiology," Vol. 2, Plenum Press, New York.
6. Smith, Allan K., U.S. Dept. Agr. Bull., ARS-71-12, April 1958.
7. Smith, Allan K., *Soybean Dig.*, **10**, No. 11, 62-65 (1959).

[Received August 4, 1960]

Removal of Fatty Soil from Glass by Surfactants and Surfactant-Builder Compositions¹

J. C. HARRIS, R. M. ANDERSON, and J. SATANEK, Monsanto Chemical Company, Research and Engineering Division, Research Department, Dayton, Ohio

Previous papers have reported radiotagged fatty soil removal from glass either by solvents or by aqueous solutions of sodium tripolyphosphate and other builders. This paper provides soil-removal data for aqueous systems of both pure and built surfactant compositions of the nonionic and alkylbenzene sulfonate types. In general, nonionics are the most effective detergents for the system fatty soil/glass; the 10-mole ethylene oxide adduct products show peak soil-removal. Nonionic surfactants appear most effective for soil removal when used in baths closely approaching their cloud-points. Though modification of hydrophobe by EO addition can affect cloud point, peak soil-removal effectiveness seems to be controlled by hydrophobe selection. Highest soil removal for the alkylbenzene series occurred with the longer alkyl chain (pentadecyl).

Admixture of surfactant and sodium tripolyphosphate provided synergistic compositions with certain 10-EO surfactants. Building of anionics markedly improved soil removal over the pure material but seldom exceeded the removal by STP alone.

PREVIOUS DATA (1,2) developed in the removal of radio-tagged tristearin from a glass substrate showed that the initial removal of cohesively-bound soil could be by dissolution if a solvent were used, and probably by emulsification if an aqueous medium not a solvent for fat (sodium tripolyphosphate solution) were used. Removal of adhesively-bound soil is more difficult than for that cohesively held, and the mechanism appears to be one of preferential displacement of soil by a more polar substance, which releases the soil from adsorption sites. In the solvent systems the more polar the solvent, the greater was the ease and completeness of soil removal. In the aqueous sodium tripolyphosphate removal system, preferential soil displacement was the significant mechanism.

The present paper is concerned with fatty soil removal in aqueous systems by a variety of surfactants and surfactant-builder compositions.

Experimental

With the exception of the following details the procedure was the same as that previously described (1,2). In addition to carbon-14 tagged tristearin, carbon-14 tagged triolein was used in certain experiments. In all cases spotted soil applications were used, as indicated in the figures. Wash temperatures are likewise indicated.

The nonionic surfactants were laboratory preparations from which the catalyst had been removed. The alkylbenzene sulfonates and the other anionics were essentially 100% active ingredient obtained by purification. The alkylbenzenes were cuts corresponding essentially to the carbon chain-lengths noted; sodium oleate and sodium lauryl sulfate (U.S.P.) were obtained from the Fisher Scientific Company.

Nonionics. The effect of molar ethylene oxide (EO) ratio at constant solution concentration upon soil removal is shown in Figure 1. Peak removal occurred at a 10-molar EO level, and while this curve is for n-dodecanol, similar curves were obtained for other adducts.

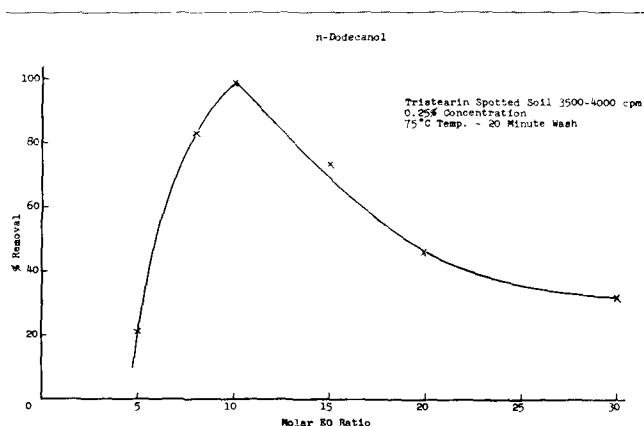


FIG. 1. Effect of Molar EO ratio on detergency.

¹ Presented at 34th fall meeting, American Oil Chemists' Society, New York, October 17-19, 1960.

Removal-concentration curves for several alkanol and one alkylphenol adduct are shown in Figures 2 and 3. These show the effect of hydrophobe upon

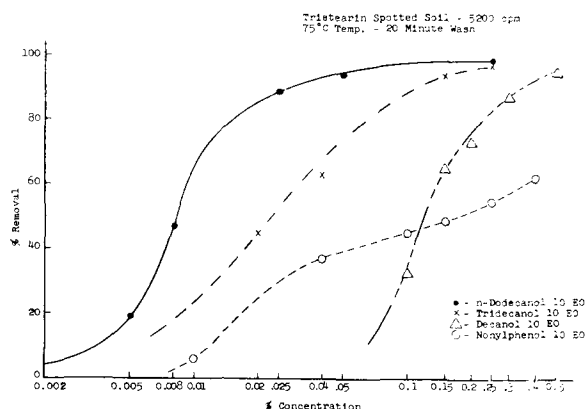


Fig. 2. Various 10-EO adducts.

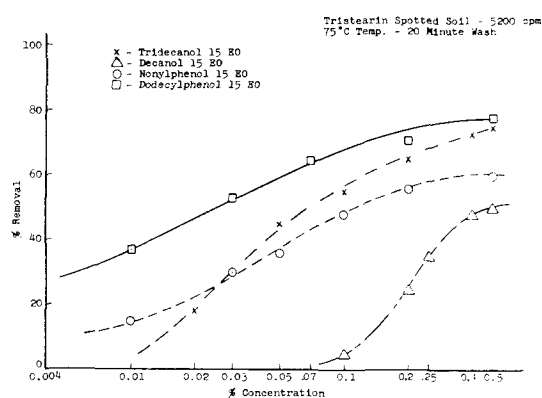


Fig. 3. Various 15-EO adducts.

removal and verify the general picture given in Figure 1 that the 10-EO ratio is a near optimum. Comparison of decanol with tridecanol (oxo) suggests the comparative hydrophobe effect, indicating that with less than optimum choice of both hydrophobe and hydrophil (decanol 15-EO, for example), even concentration increase will not adequately improve removal.

Wash-Bath Temperature Effect. A temperature of 75°C. was maintained for most of these wash baths

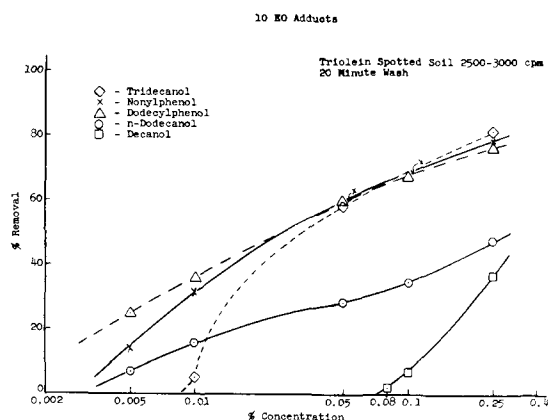


Fig. 4. Removal at 35°C.

because the melting point of tristearin is 70.8°C. However many nonionic materials have cloud points lower than this hence may not be operating at optimum concentration. Attempts at lowering the tristearin melting-point by admixture with untagged triolein failed to give comparable removal curves so triolein, liquid at room temperature, was radiocarbon-tagged and tested. Removal curves at 75°C. for the two fats were essentially identical, making it possible with triolein to reduce the wash-bath temperature without increasing the mechanical adherence of the soil.

In a series of wash tests at 35°C. the maximum removal was about 80% at a concentration of 0.25%. Considerably increased activity was obtained when these same surfactants were washed at their cloud-point temperatures (Figure 5).

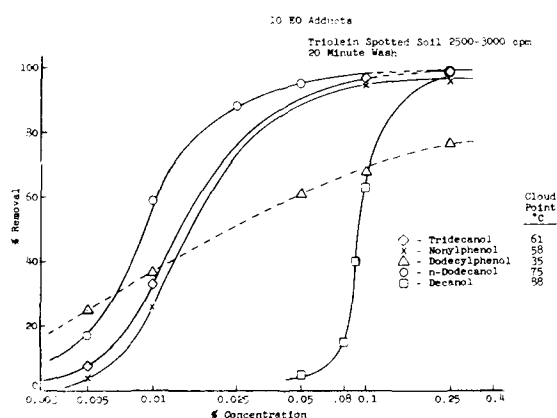


Fig. 5. Removal at cloud point.

Anionics. The effect of pH of surfactant solution upon soil removal is shown in Figure 6. Minimum removal with alkylbenzene sulfonates occurred at pH 7, with two maxima at the extremes of pH, the greater occurred near pH 3.5. When these compounds were tested alone, the pH was adjusted to the acid side; when they were used in the builder studies, it was without adjustment. Other anionics were tested at their "normal" values, alkaline for sodium oleate and at neutrality for sodium lauryl sulfate. Figure 7 shows concentration-removal curves for dodecyl-, tri-decyl-, and pentadecylbenzene sulfonates; the longer chain gave most removal. However this same figure for comparative purposes shows the relatively low effectiveness of sodium lauryl sulfate and the rather effective removal by sodium oleate.

Surfactant-Builder Mixtures. Since previous work had shown sodium tripolyphosphate (STP) as highly effective in removing soil when used alone, it was chosen for these tests, supplemented only in three cases with a 50/50 weight mixture of STP and sodium metasilicate. Figures 8 and 9 show the curves for tridecanol- and dodecylphenol-EO adducts when combined in 1:4 molar ratio with STP. Table I shows the weight/percentage active ingredient for these mixtures. The STP removal curve is shown for comparison purposes in each figure. Data were also obtained for 1:2 molar ratios of surfactant to builder, but the data did not vary markedly from those for the 1:4 ratio shown.

Figure 10 presents the data obtained with STP-

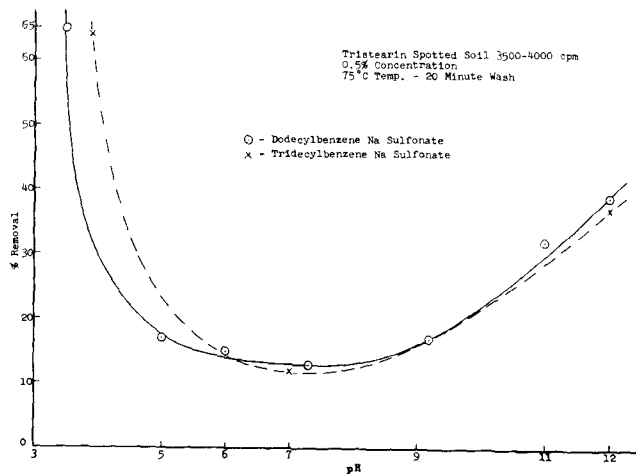


Fig. 6. Alkylbenzene Na sulfonate—pH/removal curves.

built alkylbenzene sulfonates. In this case the molar ratio of surfactant to builder was 1:2, providing the greatest soil removal. The 1:4 ratio data are not shown.

Discussion

Nonionics. It is interesting that the hydrophobes which were tested all appeared to give optimum soil-removal at an EO ratio approximating 10 (Figure 1). Though the maximum removal for other hydrophobes may be lower than that of n-dodecanol-10 EO, the greatest removal seemed to lie in this EO range. That this is related to cloud-point phenomena is discussed later. In general, adducts of 5-EO content have cloud points <0°C. (are essentially insoluble) while those of 15-EO products exceed 100°C.² The 10-EO adducts have cloud points between these extremes hence their sensitivity to temperature in soil removal. Almost without exception the EO adducts represent an approximation of a Poisson distribution as prepared, but skewing of the distribution is possible and has been encountered. In two cases, that of tridecanol and n-dodecanol-10 EO, attempts were made at separation of the several EO molar ratios, and these, when tested individually, generally verified the 10-EO ratio as giving near optimum soil removal values.

The concentration-removal curves of Figures 2 and

²The ethylene oxide adducts for convenience are discussed as 5-EO, 10-EO products, etc., without regard to the hydrophobes.

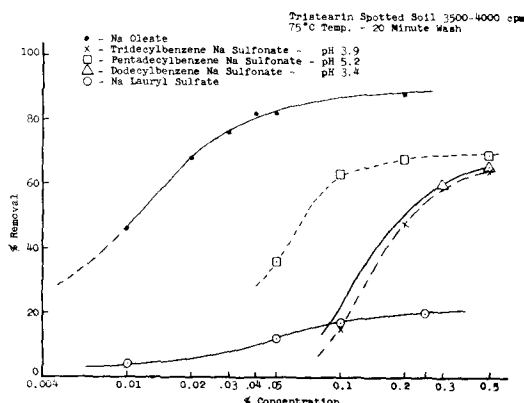


Fig. 7. Various anionic surfactants.

TABLE I
Percentage of Active Ingredient in Compositions

Surfactant	Builder mole ratio		1:4 STP/ Metasili- cate
	1:2	1:4	
Dodecylphenol— 5 EO.....	39.6	24.7
	48.8	32.3	41.7
	68.2	51.8
Tridecanol— 5 EO.....	36.4	22.2
	46.5	30.3
	67.4	50.8
C ₁₀ Benzene Na sulfonate.....	30.0	17.9
C ₁₂ Benzene Na sulfonate.....	32.1	19.1	26.2
C ₁₅ Benzene Na sulfonate.....	34.6	21.0
Na Lauryl sulfate.....	28.1	16.4	22.7

3 show the general superiority of the 10-EO ratio products over the 15- (the 5-EO products, in general, are as poor as that of n-dodecanol, Figure 1). Interestingly enough, the nonylphenol 10- and 15-mole EO products are almost identical, suggesting a broader soil-removal peak extending from near 10- to near 15-moles EO. In Figure 2 the decanol-10 EO material, when used at a high enough concentration (0.5%), closely approached 100% soil removal (only 50% removal at the same concentration for the 15-EO product), but the same removal can be attained by as little as 0.05% of the n-dodecanol-10 EO product (run at its cloud point).

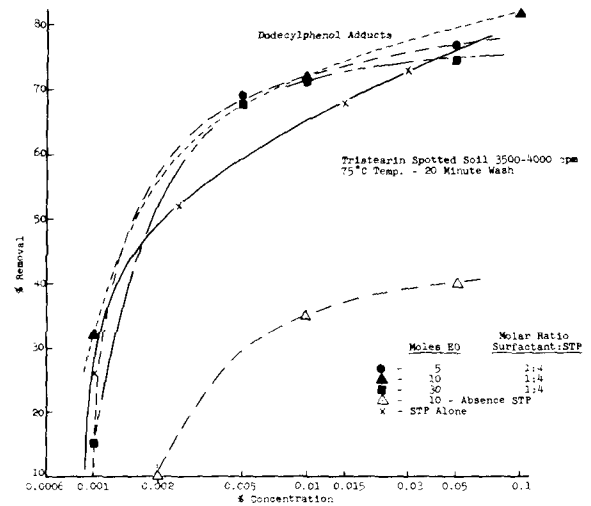


Fig. 8. Surfactant/builder mixtures.

A possible explanation, in addition to cloud point, for the maximum soil-removal values at a 10-EO level for these products is that the hydrophobes vary only mildly in apparent carbon chain-length. Experiments with shorter and longer hydrophobe chains could clarify this point.

Soil (triolein)-removal values at 35°C. for the concentration range show less than maximum values for decanol (cloud point 88°) and n-dodecanol (75°). The maxima for the other three products occurred at the largest concentration used (0.25%) but at this point were only 80%. When each product was used to wash the soiled disks at the temperature of its own cloud-point, four of the products achieved about 100% soil removal at 0.25% concentration.

These data suggest that some hydrophobes are more sensitive to changes in wash temperature than others and that a product for broad-temperature-range usage should be chosen carefully. The rule seems to be that

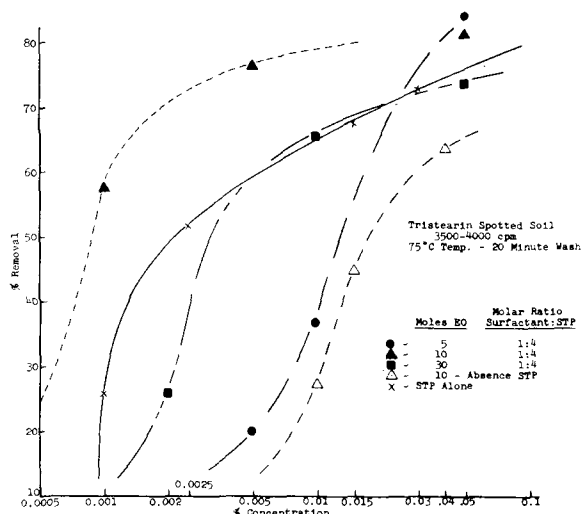


Fig. 9. Builder/tridecanol adducts.

maximum soil-removal occurs when the products are used at temperatures near their cloud-points. Also data for dodecylphenol + 10 EO suggest that low cloud-point samples are less effective than high cloud-point samples, that is, soil removal is favored by high temperature apart from temperature effect on the surfactant. These data correlate well with critical micelle concentration values, which for nonionics decrease with an increase in temperature up to the cloud point (3,4).

Anionics. It is not surprising that in Figure 6 the curves for the dodecyl- and tridecylbenzene compounds are as nearly identical as they are, for both compounds were prepared from alkylbenzene cuts. The important feature of these pH curves is that improved soil-removal can be attained by adjusting wash-bath pH to anything but near neutrality, preferably 3 to 4 or 11 to 12. These compounds are more effective surfactants either as the acid salt or in a highly alkaline medium. Interestingly enough, these curves approximate unpublished data for dodecylbenzene sulfonate for the removal of graphite from cotton. It is apparent that the aqueous medium should be altered to either condition for practical application. In bottle-washing operations the pH frequently is adjusted to near 12 while, for dairy cleaning of glass lines, the pH is reduced to near 3.5 for both maximum soil removal and bactericidal effect.

From Figure 7 it is quite apparent that pentadecylbenzene sulfonate is superior to the other alkylbenzene sulfonates; however, as side chain-length above this point is increased, solubility decreases rather rapidly, suggesting that other types of surfactants are superior for this soil/substrate system. Of the other anionics shown, sodium lauryl sulfate is quite poor while sodium oleate is relatively effective.

The foregoing data show that, for the best examples of each type of surfactant, the following decreasing order of effectiveness may be established:

- | | |
|-------------------|--------------------------------|
| n-dodecanol 10 EO | pentadecylbenzene Na sulfonate |
| tridecanol 10 EO | dodecylbenzene Na sulfonate |
| sodium oleate | Na lauryl sulfate |

If the mechanism of fatty soil-removal is one of displacement and if polarity of compound is important, the multiplicity of ether linkages of the nonionics may explain their ability to orient effectively.

No attempt will be made at an analysis of the removal curves as a function of critical micelle concentration. This will be reserved for the completion of further data.

Surfactant-Builder Mixtures. The mixtures were prepared on a 1:2 and 1:4 molar ratio of surfactant to STP builder. Though concentration-removal curves were prepared for both series, only the pertinent ones are shown. For tridecanol adducts only the 10-EO ratio showed synergistic effect; the others are essentially equal to, or poorer than STP alone. All were improved by STP addition over the surfactant alone.

For dodecylphenol adducts (Figure 8) very slight synergism by admixture with STP was found for all three EO ratios, but absent was the strong synergism for the tridecanol 10-EO product. In general, all EO ratios were improved by STP admixture, and it is indicated that this is true for more than the two hydrophobes tested.

Since the 1:2-mole ratio of anionic surfactant to STP gave useful results (the active ingredient content is too low at a 1:4 ratio), these are the only ones shown in Figure 10. In this case only the pentadecylbenzene sulfonate showed synergistic effect, but all were markedly improved through STP admixture.

Conclusions

Nonionic Surfactants. Maximum soil-removal depends upon the hydrophobe-hydrophil balance, but removal approximating 100% cannot be attained without adequate hydrophobe effective carbon chain-length. In general, maximum soil removal occurs with 10-EO adducts though solution concentrations to achieve the maximum vary widely. Some adducts cannot achieve 100% removal. In general, 5-EO adducts have cloud points $<0^{\circ}\text{C}$. and are essentially water-insoluble; 15-EO products $>100^{\circ}\text{C}$. while 10-EO products lie between these extremes. In any case these nonionics achieved maximum soil-removal at both temperatures approximating their cloud points. Lower effectiveness occurred above or below this point. The apparent correlation between critical micelle concentration and soil removal will be discussed in a later paper. These data suggest that some hydrophobes are more sensitive to wash-temperature changes than others and that a product for broad-temperature-range usage should be carefully chosen.

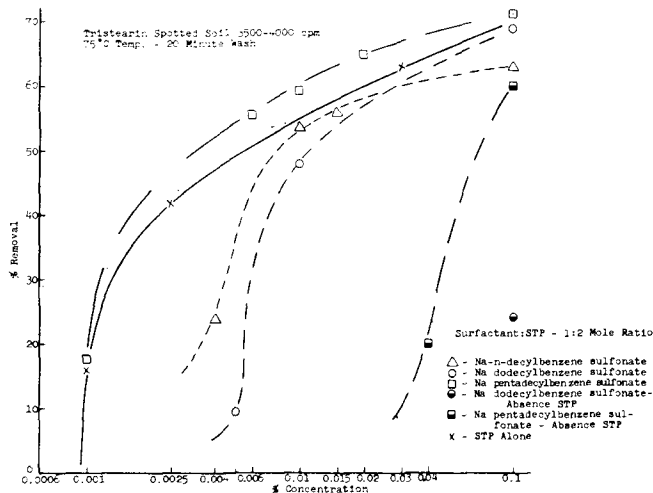


Fig. 10. Anionic/builder mixtures.

Anionics. For the anionics tested, a decreasing order of effectiveness was sodium oleate, alkylbenzene sulfonates, and sodium lauryl sulphate (practically ineffective). Alkylbenzene sulfonates showed maximum soil removal at two pH levels: 3 to 4 or 11 to 12. None was particularly effective though the pentadecyl compound was superior to those of lower alkyl chain-length.

If the mechanism of fatty soil removal is one of displacement and if polarity of compound is important, the multiplicity of ether linkages of the nonionics may afford an explanation for their effectiveness.

Surfactant-Builder Mixtures. All surfactants tested were improved by STP admixture. Synergistic effects

were found for 1:4 molar ratios of tridecanol-10 EO and STP, and slight synergism for dodecylphenol-5-, 10-, and 30-EO adducts. Of the alkylbenzene sulfonates tested, only the pentadecyl compound (1:2 ratio) showed synergism. However, without exception, admixture with STP improved soil removal over the surfactant used alone.

REFERENCES

1. Anderson, R. M., Satanek, J., and Harris, J. C., *J. Am. Oil Chemists' Soc.*, **36**, 286 (1959).
2. Anderson, R. M., Satanek, J., and Harris, J. C., *J. Am. Oil Chemists' Soc.*, **37**, 119 (1960).
3. Ginn, M. E., Kinney, F. B., and Harris, J. C., *J. Am. Oil Chemists' Soc.*, **37**, 183 (1960).
4. Nakagawa, T., Inoue, H., Tori, K., and Kuriyama, K., *Nippon Kagaku Zasshi*, **79**, 1194 (1958).

[Received August 19, 1960]

Preparation and Properties of Esters of Monohydric Alcohols and Fatty Acids of Tall Oils¹

S.T. BAUER,² PATRICIA R. GILL, and R.E. PRICE, Crosby Chemicals Inc., DeRidder, Louisiana

Esters of pure tall oil fatty acids and commercially available monohydric alcohols were prepared, distilled, and analyzed for pertinent values. The tall oil fatty acid fraction used in the esterification contained approximately 0.6% rosin acids with essentially equal distribution of fatty acids into oleic and linoleic acids. The use of various techniques, such as fast cooling by the addition of cold water to ester solution, vacuum topping before water washing, and/or use of carbon dioxide as a blanketing gas resulted in the production of light-colored ester products. These esters, low in acidic impurities and light in color, are another source of chemical intermediates for the preparation of plasticizers, cutting oils, hydraulic fluids, and lubricants.

THE PHENOMENAL INCREASE in the consumption of tall oil over the past 10 years is due mainly to the concerted efforts of the industry to improve, purify, and separate the rosin and fatty acid constituents and to convert these products into many useful derivatives. Tall oil fatty acids containing less than 1% rosin acids are now a reality and should be regarded as a mixture of essentially equal amounts of linoleic and oleic acids available for the preparation of many chemical derivatives. They, of course, readily undergo reaction at the carboxyl group to yield esters, amides, amines, soaps, etc.

This paper presents information on a series of monohydric alcohol esters prepared in the laboratory and pilot plant. We have endeavored to prepare esters of all commercially-available monohydric alcohols from methyl through eicosyl.

In this work it was realized that rosin acid impurities of the fatty acids do not esterify under normal conditions with low-boiling alcohols. This implies that tall oil ester products will always have an acid value equivalent to twice the percentage of rosin acids of the initial fatty acids.

The above has been advocated by a number of investigators as a useful method for the separation of the fatty and rosin acid constituents of crude tall oil.

Christenson and Harpt (1) separate the components of crude tall oil by esterification of the fatty acids with methyl alcohol in the presence of sulfuric acid. Rosin acids are separated as soaps in a column employing extraction naphtha as the solvent for the methyl esters. Mayer, Jacini, and Jacini (2) also use methyl esters as a means of separating the abietic acids from the fatty acids of all oil. Distillation is the means of effecting the final separation. The patent by Freeman and Gloyer (3) proposes the fractionation of tall oil by selectively esterifying the fatty acids present and contacting the mixture with furfural or other polar solvent. Esterifying agents may be methyl, ethyl, propyl, isopropyl, butyl, or various glycols. Sulfuric acid was the catalyst employed in methyl ester preparation. Litharge was used in butyl and glycol esterifications.

Most of the work on esterification of tall oil reported in the literature is concerned with the preparation of polyol esters for drying oils. Very little information has been reported on exact procedures for the preparation of monohydric esters of fatty acids. Markley (4) states, "Although the method of esterification used in the preparation of the methyl and ethyl esters of the higher molecular weight fatty acids may be stated in the general terms indicated above, the details given in the literature are surprisingly variable." Eekey (5) reports that unsaturated fatty acids esterify more slowly than saturated fatty acids. He also states that rosin acids of tall oil esterify much more slowly than the fatty acids. A temperature of at least 75°C. higher is generally required to make the rosin acids esterify at a rate comparable with that of fatty acid. Konen *et al.* (6) found that direct esterification of fatty acid with alcohol will not go unless a strong acid catalyst is present. Water formed by the reaction must be removed to cause the reaction to go to completion. Althouse *et al.* (7) prepared methyl esters of C₆-C₁₈ fatty acids by direct esterification with excess methanol and sulfuric acid as the catalyst. Propyl and isopropyl esters were

¹ Presented at the 51st annual meeting, American Oil Chemists' Society, Dallas, Tex., April 4-6, 1960.

² Present address: Picayune, Miss.