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Detergency and Foaming Properties of the System Alkylarylsulfonate-Soap-Sodium Carboxymethyl Cellulose[1]

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ALTHOUGH the literature contains numerous references to mixtures of either synthetic detergents or soap with builders and with sodium carboxymethyl cellulose, investigation of systems containing both soap and synthetic detergents has been limited.

Harris (1) and Morrisroe and Newhall (2) were among the earlier workers in this field and have reviewed the previous literature. More recently Borghetty and co-workers (3, 4) have studied such mixtures and concluded that the efficiency of soap in hard water is improved by the addition of synthetic detergents and builders. Barker (5) found that in hard water the detergency on cotton of a tallow soap or sodium laurate was improved by the addition of a nonionic detergent. Flett, Morgan, and Hoyt (6) have also discussed the complementary properties of synthetic detergents and soap and have advocated further exploration of such mixtures.

Soap as a detergent for cotton performs creditably in soft water, and built synthetic detergents have been proven satisfactory in hard water areas. It would appear that in hard water the solubilizing effect of synthetic detergents on calcium and magnesium soaps would be advantageous, particularly in view of the excellent rinsing characteristics of synthetics in this type of water.

Accordingly an investigation has been made of the system comprising an alkylarylsulfonate, a medium titer soap, and sodium carboxymethyl cellulose. It was of interest to obtain data suitable for selection of the optimum ratios of these materials for use in household laundry compositions. Since this application usually involves relatively low water temperatures, the tests were made at 120°F., using a commercially available medium titer (35°C.) soap derived from tallow and coconut oil. The alkylarylsulfonate was Kreelon 4D,[2] a sodium keryl benzene sulfonate containing 40% active agent. The sodium carboxymethyl cellulose (CMC) was Carbose D,[2] a technical grade. All tests were made in Wyandotte tap water, which is of medium hardness (96-114 ppm. total hardness as $CaCO_3$).

Detergency

The carbon soil removal and whiteness retention properties of the alkylarylsulfonate-medium titer soap-CMC ternary system were determined, using procedures previously described (7). The carbon soil removal test involves the soiling of cotton swatches from an aqueous carbon dispersion, washing in a launderometer, and determination of the amount of carbon removal by light transmission measurements on the wash liquor. The conditions are such that redeposition is minimized. In the whiteness retention test cotton swatches are agitated in carbon dispersion containing the detergent under test, and the light reflectance of the swatches is measured before and after the washing operations. The results of each of the tests are expressed relative to a standard reference detergent, Kreelon 4D.

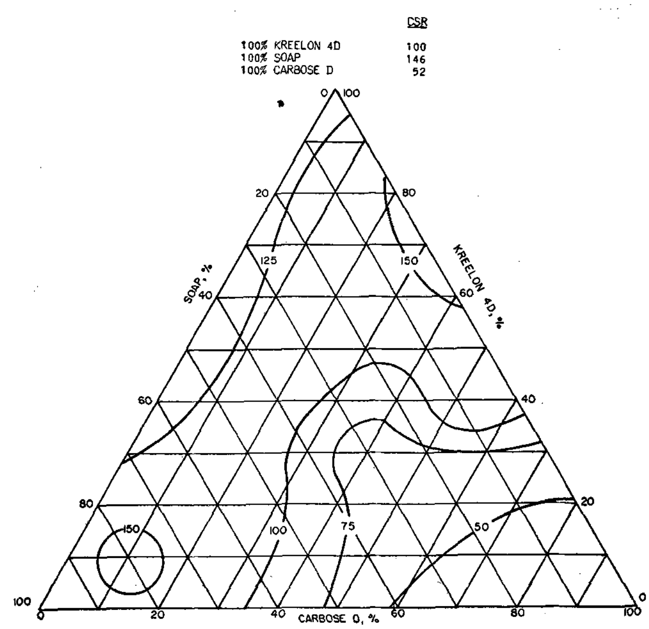

FIG. 1. Carbon soil removal characteristics in the system Kreelon 4D-medium titer soap-Carbose D.

Total concentration 0.25%, Wyandotte tap water at 120°F., all values based on Kreelon 4D 100% when tested under the same conditions.

Carbon Soil Removal. The carbon soil removal values are shown in Figure 1. Mixtures of sodium alkylarylsulfonate and medium titer soap in various proportions exhibit carbon soil removal properties such as would be expected from the arithmetical average of individual values. The addition of CMC to the alkylarylsulfonate results in improved carbon soil removal properties, but no such promoting effect occurs with the addition of CMC to this medium titer soap.

Under these test conditions the carbon soil removal properties of soap (146%) are equalled or exceeded

[1] Presented at the 43rd annual meeting, American Oil Chemists' Society, Houston, Tex., April 29, 1952.

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in two small areas representing compositions containing CMC and either a high concentration of alkylarylsulfonate and a very low concentration of soap or a very high concentration of soap and a low concentration of alkylarylsulfonate.

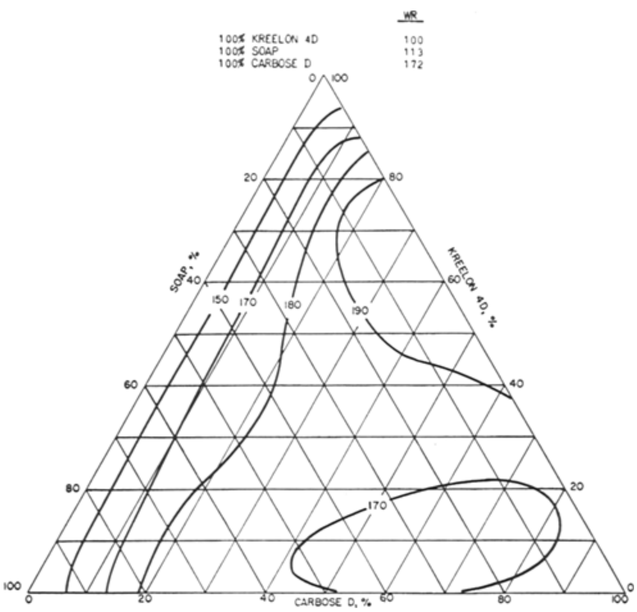

FIG. 2. Whiteness retention characteristics in the system Kreelon 4D-medium titer soap-Carbose D.

Total concentration 0.25%, Wyandotte tap water at 120°F., all values based on Kreelon 4D 100% when tested under the same conditions.

Whiteness Retention. In Figure 2 it is shown that CMC promotes the whiteness retention properties of both the alkylarylsulfonate and medium titer soap. The whiteness retention value for soap (113%) is exceeded by any ternary composition cointaining more than about 1% of CMC. Maximum values in the order of 190% are obtained within the approximate boundaries of 35-80% alkylarylsulfonate, 0-17% soap, and 16-63% CMC. At the more economically feasible CMC concentrations (1-10%) practically identical whiteness retention values are obtained with any alkylarylsulfonate-soap ratio. Thus it is evident that CMC controls the whiteness retention characteristics of this ternary system.

From these data formulations may be selected which are equal to or better than soap in both carbon soil removal and whiteness retention properties. From a detergency viewpoint the most suitable composition range for use in household laundry products would appear to be 5-15% alkylarylsulfonate, 75-85% medium titer soap, and 5-15% CMC. The amount of CMC used is dependent upon the degree of subsequent building since it is desirable to maintain a CMC concentration of 2-6% in the final built product.

Foam Characteristics

In addition to the primary requisite of adequate washing effectiveness, foaming characteristics are of particular importance in the formulation of household laundry detergents. In fully closed cylinder-type automatic washing machines, foaming volume must be limited in order to avoid cushioning effects which reduce mechanical action and to avoid leakage of foam from the machine due to the restricted space. On the other hand, in machines of the agitator type a greater volume of foam is desirable if only for psychological reasons.

The usual laboratory procedures for measuring foam do not include certain important practical factors, such as adsorption of detergent on fabric, soil loading, and simulation of agitation. Instances have been noted in these laboratories where foaming data obtained by simple shaking of the detergent solution in a graduated cylinder or by the Ross-Miles procedure (8) have failed to correlate with results obtained under actual washing conditions. Accordingly a procedure was developed which permits measurement of foam characteristics under more practical washing conditions.

The procedure involves use of a washwheel constructed of transparent plastic, which permits direct observation of foaming behavior throughout the washing cycle. The apparatus is shown in Figure 3.

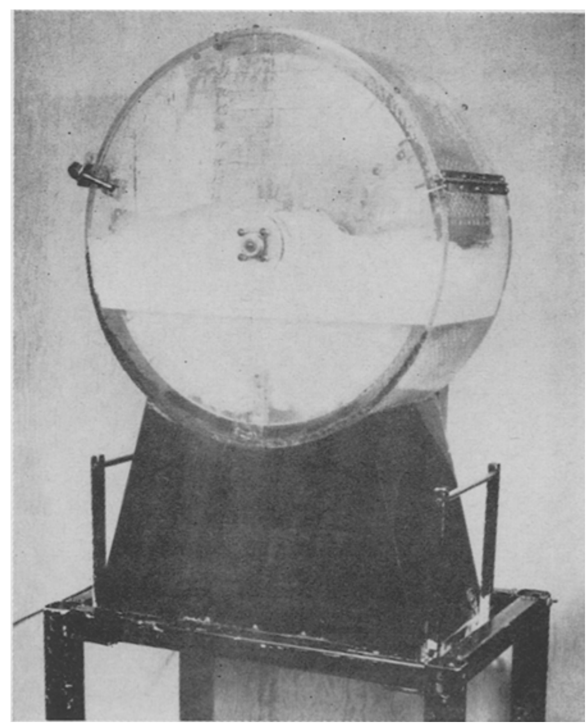

FIG. 3. Washer with transparent shell.

The washwheel consists of a perforated monel cylinder 9.25 inches wide with plastic sides 22 inches in diameter, mounted on a horizontal axis and enclosed in a plastic outer shell measuring 12 x 24 inches. Three ribs 3.5 inches high are spaced equidistant on the inner periphery of the cylinder. The cylinder reverses direction of rotation after 7 revolutions at a speed of 28 rpm. when loaded.

The washwheel is charged with 6 gallons of Wyandotte tap water at 120°F. If fabric is to be included, 8 lbs. of clean cotton fabric (sheeting and muslin) are added and the wheel rotated in order to saturate the fabric. This results in a water height of 7 inches in the wheel. The wheel is stopped at the point of reversal and the detergent added dry. Rotation is started immediately, and after 0.5 minute the wheel is stopped and 10 seconds allowed for drainage. The

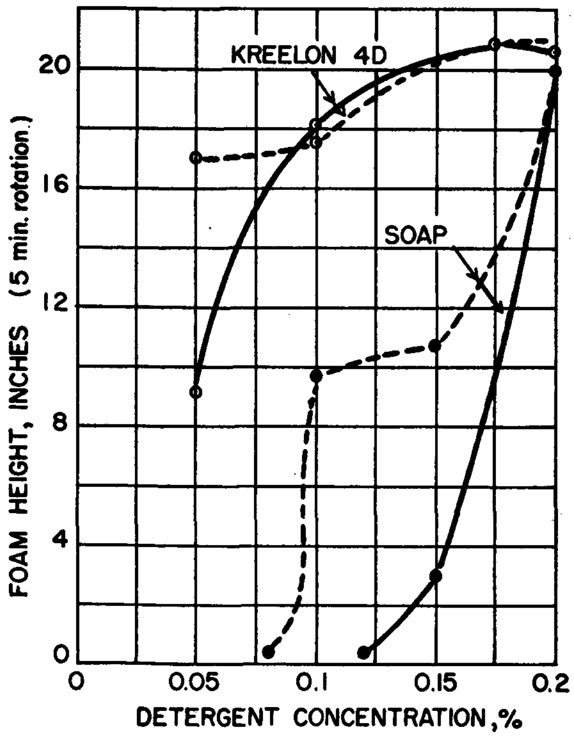

FIG. 4. Effect of detergent concentration on foam volume. ———— With fabric. - - - - - - No fabric.

height of the water and foam in the wheel is then measured by reference to a scale attached to the shell. This procedure is repeated and readings obtained at 0.5-minute intervals over 5 minutes of actual rotation time. The amount of foam is expressed as the actual height in inches derived by deducting the water height from the total height.

The range in foam height observed in four replicate determinations was three inches. A more normal range of variation, as judged from a series of duplicate determinations, is a maximum of two inches. A maximum variation of about one inch in water height is due to the position the fabric assumes after the wheel is stopped. The necessity of estimating the average foam height across the diameter of the wheel also contributes to variation. Thus the method does not provide a precise quantitative measurement but is suitable for rating on a practical basis.

It is to be noted that the limiting foam height observable by this procedure is about 18 to 20 inches, depending on the water level. In the data presented foam heights of this magnitude are reported in several instances. It may be presumed that the size of the wheel limits the foam height in these cases, in addition to the physical or chemical properties of the solution.

Effect of Detergent Concentration and Fabric. The effect of concentration of alkylarylsulfonate and of soap on foam height with and without fabric present is shown in Figure 4. The data show that the threshold concentration of this medium titer soap required to overcome the hardness of the water and produce a discernible foam after 5 minutes of machine rotation is about 0.08%. With fabric present this value is approximately 0.12%, and the difference represents the adsorptive capacity of the fabric for soap. The threshold concentration for the alkylarylsulfonate was not determined but is less than 0.05%, even with fabric present. As measured by initial appearance of foam, the effect of fabric adsorption is apparently considerably less with alkylarylsulfonate than with soap. Under these conditions the alkylarylsulfonate produces more foam than the medium titer soap at concentrations below about 0.2%.

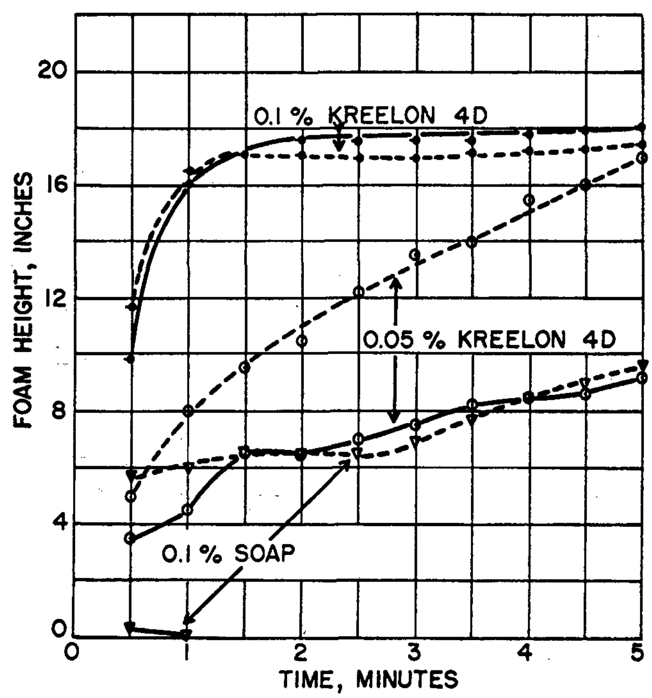

FIG. 5. Effect of fabric load on foam height. ———— With fabric. - - - - - - No fabric.

Figure 5 illustrates the effect of the fabric load on foam height throughout the 5-minute rotation cycle. At concentrations of 0.1%, alkylarylsulfonate produces more foam than this soap throughout the rotation period. The foam height is reduced to zero on addition of fabric to the soap solution while the effect is negligible in the case of the alkylarylsulfonate at this concentration. At 0.05% of alkylarylsulfonate, loading with fabric reduces the foam height significantly, to a level essentially the same as that of 0.1% soap without a cloth load. It is obvious that when working at the lower concentrations prediction of foaming characteristics for laundry applications based on tests in the absence of fabric could be quite misleading.

It has been determined that addition of the detergent dry to the wheel provides essentially the same foam height after the first minute of rotation as obtained by use of a stock solution.

Effect of Sodium Carboxymethyl Cellulose. The effect of CMC on the foaming characteristics of soap and alkylarylsulfonate is shown in Table I. The slight effects due to CMC were judged to be of no practical significance. Because of this and the fact that the amount of CMC used in a detergent composition is dependent on type and degree of building, CMC was omitted from subsequent foam studies.

Alkylarylsulfonate-Soap Mixtures. Foaming characteristics of mixtures of alkylarylsulfonate and soap in the presence of fabric are shown in Figure 6. At

TABLE I
Effect of CMC on Foam Height

Total Conc.	Detergent composition, parts			Foam height, inches, after 5 min. rotation	
	Kreelon 4D	Medium titer soap	Carbose D	No fabric	With fabric
%					
0.09	90	0	0	20.0	19.6
0.10	90	0	10	18.6	18.0
0.09	70	20	0	18.7	16.2
0.10	70	20	10	15.6	14.0
0.09	0	90	0	1.6	0
0.10	0	90	10	4.2	0

0.1% total concentration, inclusion of more than 25% soap results in drastic reduction in foam height. This is undoubtedly partially due to the adsorption and hard water effects noted previously. At 0.2% total concentration, foam height decreases with increase in soap content to a minimum at about 60% soap, and then increases. A similar but less pronounced minimum was noted at 0.2% total concentration when no fabric was present. This effect disappeared entirely when using distilled water, even with fabric present.

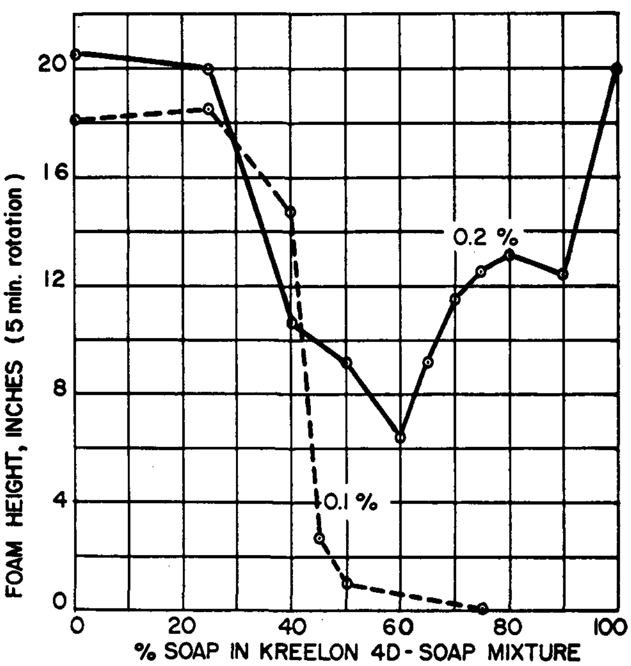

FIG. 6. Foam characteristics of Kreelon 4D-medium titer soap mixtures.
With fabric load.

If the total concentration is increased in the presence of hard water, the minimum disappears at a total concentration of 0.23%. With both fabric and hard water, the concentration necessary to flatten the curve is 0.27%.

Discussion

In selection of the proportions of alkylarylsulfonate, medium titer soap, and CMC for inclusion in built household laundry detergents, adequate detergency must be provided as well as the desired foaming characteristics and other requisites. From the point of view of whiteness retention, inclusion of approximately 5 to 15% of CMC in the organic portion of the formulation is clearly indicated. This is consistent with CMC requirements for soil removal and does not affect foaming properties appreciably. For optimum soil removal, the data indicate that the ratio of medium titer soap to alkylarylsulfonate should be approximately five to one.

The foaming characteristics of compositions having this ratio, as compared with those of compositions having a high alkylarylsulfonate content, are influenced to a greater extent by factors of detergent concentration, water hardness, and absorption on fabric.

In water of medium hardness, with ordinary solution to cloth ratios, and at relatively low use concentrations, a five to one ratio of soap to alkylarylsulfonate yields the moderate foaming volume desired in cylinder type machines. The concentration effect can overshadow the other factors and by regulation can provide any desired foam level ranging from practically none to overflowing.

For use in agitator type of machines, the high foam levels are generally desirable. The necessity of high detergent concentrations, as well as critical dependence of foam height on concentration, can be avoided by decreasing the soap to alkylarylsulfonate ratio. In the latter case the depreciating effects of water hardness and fabric adsorption are minimized and the amount of detergent required for a given foam height is reduced. From the standpoint of carbon soil removal the use of high proportions of alkylarylsulfonate results in compositions outside the optimum range in the ternary system as shown in Figure 1. The values however of compositions having approximately three parts alkylarylsulfonate to one part soap, as are desirable from the foaming standpoint, are such that ample soil removal properties are attainable by proper choice of builders.

Summary

A study has been made of the detergency and foaming characteristics of a ternary system comprising a sodium alkylarylsulfonate, a medium titer soap derived from tallow and coconut oil, and sodium carboxymethyl cellulose under average conditions prevailing in household laundering.

The carbon soil removal and whiteness retention properties of unbuilt soap are equalled or exceeded in compositions containing approximately five parts soap to one part alkylarylsulfonate, with a minor portion of CMC.

Measurements made in a transparent cylindrical washer indicate that the decrease of foam height due to adsorption on fabric and hard water is much greater with soap than with alkylarylsulfonate. This results in greater foam volumes with alkylarylsulfonate than with soap at concentrations less than 0.2%, in water of hardness equivalent to 96-114 ppm. $CaCO_3$.

Sodium carboxymethyl cellulose, when used with soap and alkylarylsulfonate in the proportions desirable for improvement of detergency, does not affect foaming properties significantly.

When soap is the major ingredient in mixtures of soap and alkylarylsulfonate, foam height is critically dependent on concentration. When alkylarylsulfonate predominates, high foam levels are obtainable at low concentrations.

The data reported permits selection of compositions from the ternary system for formulation with builders such that excellent detergency characteristics may

be obtained under average conditions prevailing in household service, with high foaming characteristics as desired for agitator-type machines, or with moderate, controllable foaming for cylinder machines.

Acknowledgment

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Application of Urea Complexes in the Purification of Fatty Acids, Esters, and Alcohols. III.[1] Concentrates of Natural Linoleic and Linolenic Acids[2]

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THE preparation of concentrates of polyunsaturated fatty acids (or methyl esters) which have the same configuration as that in the vegetable oils from which they are derived is an important and basic problem in fat chemistry. By far the bulk of fundamental research on these compounds in the past, particularly prior to 1945, was conducted on polyunsaturated substances prepared by bromination-debromination procedures since it was assumed that debromination products were essentially the same as the natural acids of the vegetable oils from which they were derived. Ultraviolet and infrared spectrophotometric methods for examining polyunsaturated materials however have been mainly responsible for showing that this assumption is not correct and that polyunsaturated materials prepared by bromination-debromination procedures, even though theoretical iodine numbers are obtained, may contain substantial amounts of isomers.

Natural linoleic acid (*cis,cis*-9,12-octadecadienoic acid) has apparently been isolated in pure form by Brown and coworkers (2, 3) by repeated low temperature fractional crystallization of the mixed acids from a number of vegetable oils. Natural linolenic acid (*cis,cis,cis*-9,12,15-octadecatrienoic acid), on the other hand, has not been obtained in the pure state by the same technique; the highest concentration reported is 88% (10). Riemenschneider and coworkers (4, 5, 8) however, employing adsorption fractionation on silicic acid, have recently prepared pure methyl esters of natural linoleic, linolenic, and other polyunsaturated acids.

Adsorption fractionation to prepare pure fatty acids is, at present, still limited to relatively small scale laboratory operations, it is time-consuming, and relatively large amounts of solvent are required. In this technique it is decidedly advantageous to employ mixtures which are as rich as possible in the component being sought so that the already limited adsorptive capacity of laboratory columns is not consumed in the removal of a large amount of unwanted components. Where the highest purity products are required, the urea complex separations to be described in this paper are an excellent preliminary concentration step.

As a logical extension of earlier investigations (12, 13), we have successfully applied urea complex precipitation technique to the preparation in good yield (50-90%) of concentrates of natural linoleic and linolenic acids (purity 66-95%) from oils rich in these acids, taking advantage of the preferential precipitation of the urea complexes of the saturated and monounsaturated acids from corn oil fatty acids, and the preferential precipitation of saturated, monounsaturated, and diunsaturated acids from linseed oil fatty acids or perilla oil fatty acids. The urea complex separation technique minimizes or obviates some of the disadvantages of the low-temperature crystallization or adsorption techniques discussed earlier in this paper. In the urea complex separation techniques described in this paper operations are usually conducted between room temperature and the boiling point of methanol, and occasionally at 0°C. Disadvantages of the urea complex separation technique have been discussed in our previous papers (12, 13).

Some work has been published on the use of urea complexes in the preparation of concentrates of polyunsaturated acids and methyl esters from linseed and corn oils. Newey and coworkers (6) reported the concentration obtained by a single urea precipitation, based solely on iodine number, without demonstrating the practical limit of concentration which could be achieved by a repetition of the urea treatment. Furthermore the composition of the starting materials and the concentrates were not reported so that it is difficult to assess the efficiency of the separations. Schlenk and Holman (9) reported similar data and, in addition, stated that two preparations of methyl linoleate, iodine number 168 and 173, were obtained from corn oil methyl esters in 23% and 14% yields, respectively. Unfortunately operational details, such as the quantity of urea and methanol and the number of urea

[1] The preceding papers in this series are references 12 and 13.

[2] Presented at the Fall Meeting of the American Oil Chemists' Society, Cincinnati, O., Oct. 20-22, 1952.

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