erization, it is questionable whether the small amount of nonconjugated trienoic acid reported in tobacco seed oil and other similar oils (1) is due to simple oxygenated products of autoxidation. This is suggested in view of the fact that the nonconjugated triene is not completely eliminated by countercurrent extraction of the autoxidized fraction in the case of autoxidized corn oil esters. It is possible however, that some of this conjugated triene absorption may result from the alkali isomerization of other products of autoxidation which cannot be separated from the unoxidized fraction by the procedure outlined.

Nevertheless the major interferences in the spectrophotometric determination of fatty acids caused by the presence of the products of autoxidation can be eliminated by countercurrent extraction of the oxygenated fraction. The method of extraction is simple and applicable to glyceridic fats by performing a preliminary interesterification with methyl alcohol. Thus, by means of this method of separation, the scope of the spectrophotometric method of fatty acid analysis is extended to include fats that have undergone some autoxidation.

Summary

The nature and extent of the interferences by autoxidized fatty acids in the application of spectrophotometric methods of fatty acid analysis are described.

A simplified countercurrent extraction procedure for the quantitative removal of the oxygenated fraction of autoxidized fatty acid esters was developed. By means of a preliminary interesterification process it was found possible to apply the extraction procedure in the analysis of autoxidized glyceridic fats.

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Detergency Properties of Sodium Carboxymethyl Cellulose-Soap-Builder Systems

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AN OUTGROWTH of the general acceptance of sodium carboxymethyl cellulose for improvement of detergency properties of synthetic detergent compositions has been the investigation of its effect on the detergency properties of systems containing soap instead of synthetic detergents. To mention one such investigation, Bayley *et al.* (1) have reported on the effect of sodium carboxymethyl cellulose (CMC) on the suspending power of soap and soap-builder solutions. It is the purpose of this paper to present data on the effect of sodium carboxymethyl cellulose on both soil removal and whiteness retention properties of two soap-alkaline builder systems. This work may generally be considered a supplement to previously published work from these laboratories involving synthetic detergent-alkaline builder-CMC systems (2).

The principles, precision, and details of the detergency test methods used in this work have recently been published (3).

Materials

The analyses and other identifying characteristics of the test materials used in this work were as follows:

Soap. A commercial grade, powdered 92% high titer (42°C.) soap.

Carbose D[1] *Lot No. C-3788-F.* A technical grade of sodium carboxymethyl cellulose. This sample of carbose differs in analyses and detergency properties from the lots of carbose used in previously reported work (2). Hence the data presented, while quantitative and comparable for the systems under study, are not directly comparable with the previous data.

Soda Ash. A commercial grade containing a minimum of 99.5% Na_2CO_3.

Modified Soda.[2] A detergent grade meeting ASTM specifications with an average Na_2CO_3-$NaHCO_3$ ratio of 1:1.39 by weight.

Detergency in the Systems Soap-CMC-Alkaline Salts

Carbon soil removal and whiteness retention characteristics were determined on systems containing soap, CMC, and either soda ash or modified soda. Carbon soil removal and whiteness retention tests were conducted in distilled water at 140°F. and all data were calculated relative to soap as a standard having an assigned value of 100%.

The relative proportion of each component of each system was varied between the limits of 0 to 100% as the total concentration in the test solution was maintained at 0.25%. Triangular coordinate graphs of the detergency values of each three-component system were plotted, using 180 datum points of which a minimum of 36 were determined and the remainder obtained by interpolation. The interpolated values were obtained from curves drawn through points which were plotted, using as the abscissa the composition of a binary system or that of a ternary system in which the concentration of one component was kept constant, and as the ordinate the determined carbon soil removal or whiteness retention value. For ease of comparison only iso-detergency lines at various levels are presented, and discussion will be confined primarily to soap-CMC and soap-builder-CMC systems.

Although the effect of carbose has been studied over the range of 0 to 100%, economic considerations limit the use of CMC to relatively low concentrations, and it is these areas of the diagrams that are of major interest in detergent applications.

[1] Carbose D ®, produced by Wyandotte Chemicals Corporation, Wyandotte, Mich.

[2] Yellow Hoop, ®, produced by Wyandotte Chemicals Corporation, Wyandotte, Mich.

Carbon Soil Removal Data. The carbon soil removal properties of the two systems are shown in Figures 1 and 2. At a total concentration of 0.25% the carbon soil removal properties of the soap-builder system decrease with increase in builder content. As CMC is added to the soap-builder system, the carbon soil removal properties increase to a maximum and then decrease. With soda ash, maximum soil removal values of 130% or slightly greater are obtained within the approximate limits of CMC 20 to 50%, soap 28 to 55%, and soda ash 5 to 45%.

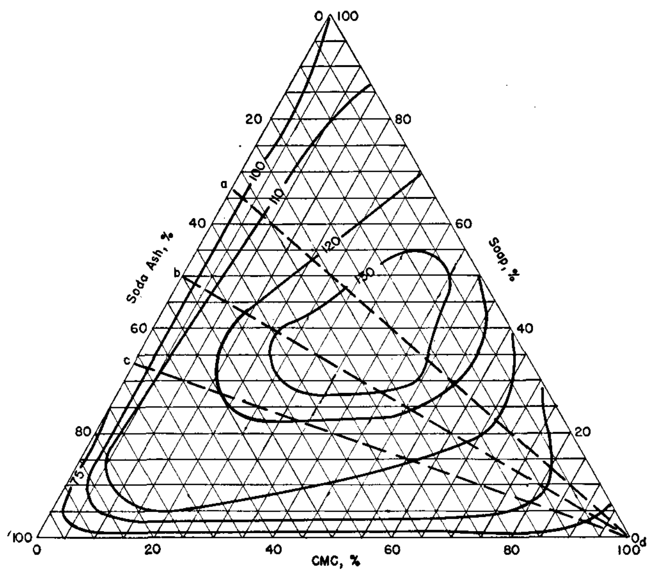

FIG. 1. Carbon soil removal characteristics in the system soap-CMC-soda ash. Tests made at 0.25% total concentration in distilled water at 140°F. All values based on soap = 100%.

With soap and modified soda, the addition of CMC increases the carbon soil removal properties to 120% of soap alone, and the iso-detergency lines have the same general shape as that obtained with soda ash. Maximum soil removal in this system is found within the approximate boundaries of 30 to 50% CMC, 50 to 70% soap, and 0 to 1% modified soda. Figure 1 shows that for the same detergency level (120%) as obtained with modified soda the soda ash system boundaries approximate 30 to 50% CMC, 22 to 70% soap, and 0 to 55% soda ash. This would appear to indicate a greater tolerance for soda ash than for modified soda in soap-CMC systems, or conversely, a more pronounced promoting effect from CMC in soap-soda ash than in soap-modified soda systems.

At varying absolute proportions of soap plus builder in ratios commonly encountered in commercial practice, 2:1, 1:1, and 1:2, carbon soil removal values of formulations having inversely varying proportions of CMC are found respectively along lines ad, bd, and cd in Figures 1 and 2. With either builder at CMC concentrations below about 5%, the carbon soil removal properties are essentially the same within the above mentioned soap:builder ratio limits. Thus it is evident that small amounts of CMC increase builder tolerance without sacrifice in soil removal properties. The use of CMC also permits the extension of builder concentration to considerably more than that commonly used with soap. For example, a composition comprising approximately 15% soap, 82% soda ash, 3% CMC has a carbon soil removal value about 135% of that obtained with 15% soap and 85% soda ash and is equal to unbuilt soap. Since carbon soil removal properties increase with increase in concentration of detergent (4), the addition of small amounts of CMC permits use of lower concentrations of soap-builder mixtures to obtain the same results as possible at higher concentrations in the absence of CMC or, when used in equal concentrations (e.g., 0.25%), CMC gives higher soil removal levels.

The carbon soil removal properties of soap-CMC mixtures are presented in Figure 3. With increasing CMC content in the soap-CMC system there is an increase in carbon soil removal properties to a maximum level of about 120% at 40% CMC concentration. Beyond this concentration the values decrease to the 63% level obtained with CMC alone.

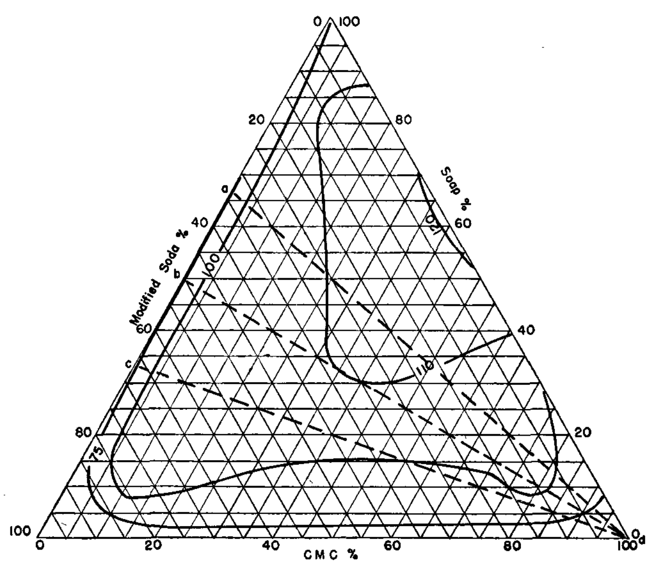

FIG. 2. Carbon soil removal characteristics in the system soap-CMC-modified soda. Tests made at 0.25% total concentration in distilled water at 140°F. All values based on soap = 100%.

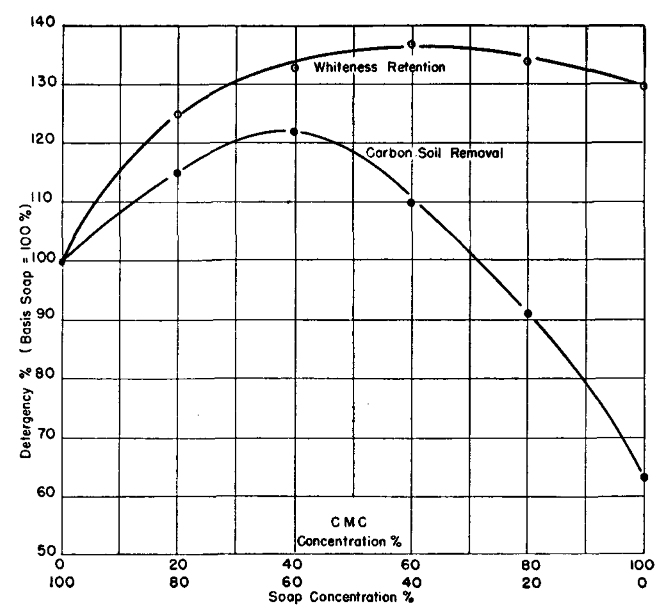

FIG. 3. Effect of CMC on detergency properties of soap. 0.25% total concentration.

Whiteness Retention Data. The results of the whiteness retention tests on the two systems are shown in Figures 4 and 5. In the two-component soap-builder system a decrease in whiteness retention properties occurs with increase in builder content. This effect is greater with soda ash than with modified soda as has been often observed and reported in previous work.

The addition of CMC to the soap-builder systems results in an increase in whiteness retention properties to values for both builder systems of about 135%, CMC alone at 0.25% concentration having a value of 130% of soap. At a given soap : builder ratio small amounts of CMC provide a substantial increase in suspending power over that of built soap. For example, at 1 : 1 soap to builder ratio the whiteness value is 30% for the soap built with soda ash. The substitution of CMC for 3% and 5% of the built soap gives values of 50% and 65% respectively.

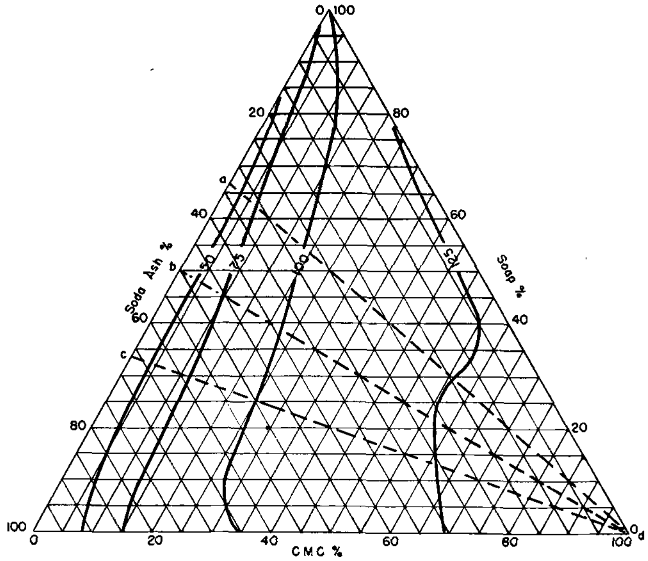

FIG. 4. Whiteness retention characteristics in the system soap-CMC-soda ash. Tests made at 0.25% total concentration in distilled water at 140°F. All values based on soap = 100%.

At the lower whiteness retention levels, the modified soda system requires slightly less CMC to attain a given level than does the soda ash system. The decrease in whiteness retention properties with increase in builder content of the two-component soap-builder system is practically eliminated for common soap: builder ratios by the use of small amounts of CMC as shown by the parallelism of "iso-detergency" lines with the builder axis in Figures 4 and 5. The same effect is noted for carbon soil removal properties, and the practical implication is that the use of CMC eliminates the need for accurate adjustment of the soap: builder ratio.

The effect of CMC on the whiteness retention properties of soap is shown in Figure 3. The addition of CMC with corresponding decrease in soap content results in a marked increase in whiteness retention

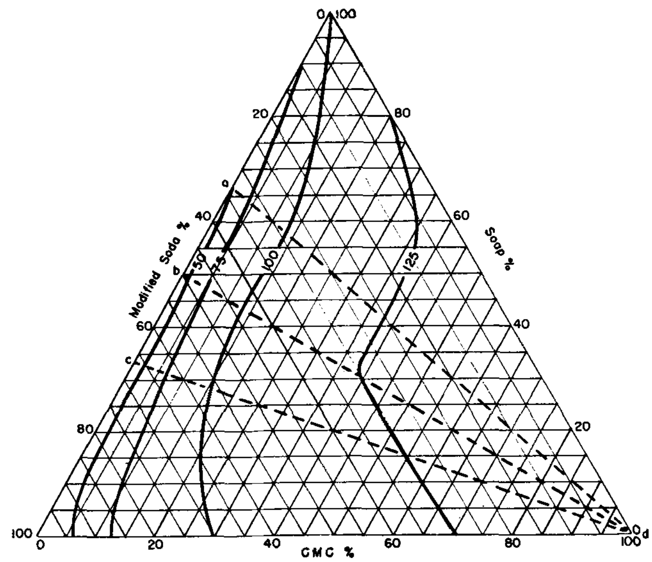

FIG. 5. Whiteness retention characteristics in the system soap-CMC-modified soda. Tests made at 0.25% total concentration in distilled water at 140°F. All values based on soap = 100%.

properties to a maximum value of 137% of soap at about 60% CMC content. Beyond this CMC concentration the values drop to the 130% level obtained with Carbose alone.

Summary

Data have been presented which illustrate the detergency properties of soap-sodium carboxymethyl cellulose-builder systems. Practical considerations limit use of CMC to the lower concentrations, and it has been shown that at sodium carboxymethyl cellulose concentrations of 5%, or even less, builder tolerance is increased without sacrifice in soil removal properties. At CMC concentrations above 3% the soil removal properties of the ternary systems under study are increased above that of soap alone except in the case of very high builder content. Within common soap: builder ratios the whiteness retention properties of the system are substantially increased by the addition of CMC. Both soil removal and whiteness retention properties of unbuilt soap are also increased by the addition of small amounts of CMC.

Acknowledgment

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