The Relation of Temperature and Concentration to Detergency in Systems of Sodium Carboxymethyl Cellulose, Sodium Alkylaryl Sulfonate, and Alkaline Detergent Builders*

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Introduction

THE production of and interest in sodium carboxymethyl cellulose[1] has received impetus recently from the successful application of certain types of this material in the field of detergency. In an earlier paper (1) it was shown that a sodium alkylaryl sulfonate alone or built with alkaline salts may be promoted with sodium carboxymethyl cellulose to give detergency values on cottons greater than those obtainable with high grade soaps commonly used in commercial laundering. Emphasis was given to systems containing a sodium alkylaryl sulfonate because at present this type of synthetic detergent when activated exhibits suitable detergent qualities, is produced at such a price that it can be considered for commercial laundering, and is available in large quantities from a number of suppliers.

In the present work similar systems of sodium alkylaryl sulfonate, sodium carboxymethyl cellulose, and inorganic builders have been investigated to determine the relationship between detergency and temperature, and detergency and concentration. Systems having considerable difference in composition but approximately the same carbon soil removal values at one typical set of conditions were chosen for comparison. For reference purposes unpromoted systems of synthetic detergent and builder have also been included. One of the principal questions to be resolved by this work was what variation in detergency might be expected between such systems when concentration or temperature was varied.

The Measurements of Detergency

For the purpose of this study the washing of cottons has been the sole consideration. This material comprises the great bulk of commercial laundry work and retains soil far more tenaciously than woolens and synthetic fabrics; therefore it is practically and experimentally an entirely suitable test fabric.

In these laboratories detergency with respect to cottons is broken down into two separate factors. The one—soil removal—is an expression of the capacity of a detergent solution to remove soil from a soiled fabric; the second — whiteness retention — is an expression of the capacity of the detergent solution to prevent a colloidal carbon soil from depositing and adhering to an unsoiled fabric.

The methods used for these measurements have previously been reported in detail (1). In view of this description, it will suffice here to describe briefly several revisions which have been made since that time in the whiteness retention test method. An unfinished muslin is now available,[2] and by its use considerable time is saved because of the elimination of the desizing step. The solutions are now prepared for this test by weighing 2.500 g. of the material to be tested and transferring it to a 1-liter volumetric flask. Sufficient distilled water is added to effect solution followed by 50.0 ml. standard carbon black dispersion. The solution is made up to volume with distilled water and thoroughly mixed. This modification eliminates several weighing and pipetting steps involving small quantities of material.

The foregoing revisions chiefly reduced the procedure time. This saving is partially compensated by the following revisions which were made for the purpose of decreasing manual and random error. Before the cloth panels are added to the test jars, they are presoaked in distilled water for one minute after which the excess water is wrung out by hand. The test period in the Launderometer is increased from 15 minutes to 30 minutes since investigation has shown the latter fell on a much less critical point of the soil deposition-time curve than the former.

The whiteness retention test pieces are now mechanically rinsed in an apparatus (Figure 1) consisting of a Gyrosolver[3] holding four 1-liter Erlenmeyer flasks each equipped with outlets to the drain and inlet connections to receive water from individual 3-liter distilled water reservoirs. The connections to the 1-liter flasks include fused-in 8-mm. O.D. glass fittings, the outlet being two inches above the bottom of the flask and the inlet 1.5 inches above the bottom of the flask and directly opposite the outlet connection. The flow of distilled water is controlled by suitable capillary tubes (approximately 2-mm. I.D., depending upon elevation of reservoirs) in each of the four feed lines so that from 5 to 6 minutes is required for the 3-liter reservoirs to drain through the 1-liter rinsing flakes. After rinsing, the test pieces are pressed dry between clean cover cloths using a Prosperity pony press operated on 80 lb. steam pressure.

Because of the above-mentioned changes the whiteness retention results contained in this paper are not comparable on an absolute basis with those previously reported (1) for the same formulations. Within each paper values have been determined under identical conditions and comparative results between formulations are the same for both papers. Present results are higher than those previously found chiefly because of the more vigorous rinsing technique. In an earlier paper (1) the precision of the methods was reported to be such as to give a per cent mean deviation of ± 3.1 for the carbon soil removal test and ± 1.8 for the whiteness retention. Extended work confirms the former value but it is necessary to revise the latter, which is believed to be of the order of ± 5.0. These values are based on tests of pure synthetic detergents as well as mixtures of alkalies, detergents, and Carbose, made by several operators and in two laboratories. Better precision can be obtained by one highly trained tech-

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[1] The chemistry of this material has been discussed by Höppler (2) and the properties, manufacture, and various uses reviewed by Hollabaugh, *et al.* (3).

[2] Bleached unfinished Indian Head Muslin, manufactured by the Nashua Manufacturing Co., Nashua, New Hampshire.

[3] Fisher Scientific Co., Pittsburgh, Pa.

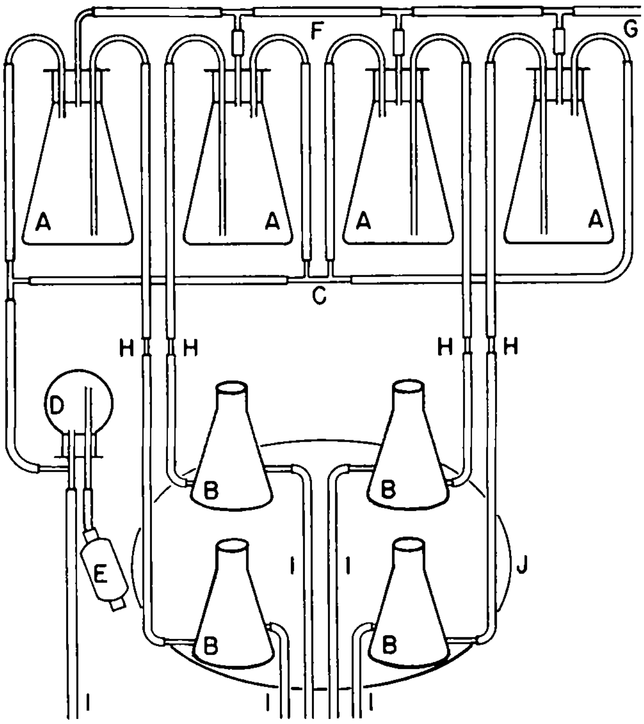

FIG. 1. Mechanical rinsing device used in the whiteness retention test.

A. 3-liter Erlenmeyer reservoir flasks.
B. 1-liter Erlenmeyer rinsing flasks with fused-in fittings.
C. Breather manifold for reservoir flasks.
D. 250-ml. round bottom flask with assembly for venting air and water from breather manifold.
E. Pressure bulb for starting flow of rinse water.
F. Distilled water intake manifold.
G. From distilled water supply.
H. Capillary tubes in rinse water flow lines.
I. Lines to sink.
J. Table of Gyrosolver.

nician doing comparative evaluation work in one laboratory, and under these conditions the higher order of precision is of course valid.

Unless otherwise stated, all data for both carbon soil removal and whiteness retention are expressed in per cent, and relative to a value of 100% for the detergency of a standard type detergent[4] used at 0.25% concentration in distilled water at 140°F.

Test Materials

The analyses and other identifying characteristics of the materials used in this work are given below:

Soda Ash. A commercial grade analyzing as follows: Na_2CO_3 99.5%; NaCl 0.4%; Na_2SO_4 0.05%; insolubles 0.01%; Fe 0.002%.

Modified Soda. A detergent grade with an average Na_2CO_3-$NaHCO_3$ ratio of 1:1.39 by weight.[5]

Carbose D ® Lot No. C-2225-E.[6] A lot of one of the several technical forms of sodium carboxymethyl cellulose. It contains approximately 70% sodium carboxymethyl cellulose by difference and shows 1% insolubility upon filtration. In all of the work reported in this paper this particular lot (referred to hereafter simply as "Carbose") was used. The data offered should be accepted as indicating the trend of improvement that may be obtained in using sodium carboxymethyl cellulose in conjunction with synthetic detergents but not indicating the maximum detergency promotion which it is possible to obtain since types of Carbose having greater detergency promoting properties have already been developed.

Kreelon 4D[7] ®. A sodium alkylaryl sulfonate type of synthetic detergent having the following approximate composition: organic sulfonate 40%; inorganic salts 60%.

Detergent Formulations

The main portion of this investigation was carried out using six formulations differing in composition but having approximately the same carbon soil removal properties when tested at a concentration of 0.25% in distilled water at 140°F.

Formulations A, B, and C contain Kreelon 4D, modified soda and Carbose, A containing a relatively high percentage of Kreelon 4D, B a relatively high percentage of modified soda, and C a relatively high percentage of Carbose. Formulations D, E, and F correspond in order to A, B, and C but contain soda ash in place of modified soda. The composition of these and other formulations used are given in Table I along with the basic detergency values obtained at the standard conditions of 0.25% detergent concentration in distilled water at 140°F.

TABLE I
Composition of Built and Promoted Synthetic Detergent Formulations and Their Basic Detergency Values at Standard Conditions

Formulation	Kreelon 4D, %	Carbose, %	Modified Soda, %	Soda Ash, %	Relative Carbon Soil Removal, %*	Relative Whiteness Retention, %*
A	70	15	15	....	166	329
B	35	15	50	....	158	310
C	35	50	15	....	159	384
D	70	15	....	15	163	315
E	35	15	....	50	163	280
F	35	50	....	15	163	374
G	70	....	....	30	102	50
H	35	....	....	65	98	34
K	100	....	....	....	100	100

* Detergent concentration 0.25% in distilled water at 140°F.

Formulations G and H include no Carbose and contain respectively large percentages of Kreelon 4D and of soda ash. Formulation K is simply Kreelon 4D unmodified. Formulations G and H were so chosen as to have approximately the same carbon soil removal properties as Kreelon 4D—that is 100% relative carbon soil removal—under the standard conditions of 0.25% concentration at 140°F. Formulation G contains the same percentage of synthetic detergent as Formulations A and D; and H contains the same percentage of synthetic detergent as B, C, E, and F.

In summary, we have within this group of materials a number of built and promoted synthetic detergent formulations of identical carbon soil removal properties under one set of conditions; built synthetics, and built and promoted synthetics of the same synthetic detergent content but different carbon soil removal properties; and built and unbuilt synthetics with the same carbon soil removal properties under one set of conditions but different synthetic detergent content.

The Carbose-promoted formulations were selected to provide practical levels of detergency exceeding somewhat that afforded by a typical unbuilt high titer soap used in commercial laundering. The latter by these tests gives a relative carbon soil removal

[4] The standard type detergent used in these laboratories is Kreelon 4D ®.

[5] Yellow Hoop ®, manufactured by Wyandotte Chemicals Corporation, Wyandotte, Mich.

[6] Produced by Wyandotte Chemicals Corporation, Wyandotte, Mich.

[7] Produced by Wyandotte Chemicals Corporation, Wyandotte, Mich.

value of 147% and a relative whiteness retention value of 217%.

Detergency as a Function of Concentration in Built and Promoted Synthetic Detergent Systems

In investigating the relation of concentration to detergency—both carbon soil removal and whiteness retention—a temperature of 140°F. was chosen, this being the standard temperature used for general comparisons of laundry detergent formulations in these laboratories. The series of concentrations studied (0.05% to 0.5%) largely covers the range of effective or economical levels likely to be encountered in commercial usage.

Carbon Soil Removal as a Function of Detergent Concentration. The carbon soil removal values for the built and promoted synthetic detergent formulations are plotted as a function of detergent concentration in Figures 2 and 3 and for the unbuilt and soda ash-built synthetic detergent formulations in Figure 4.

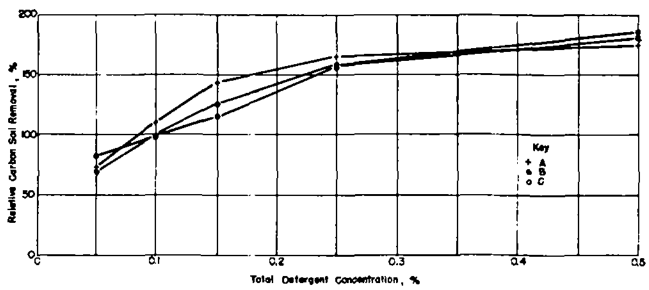

FIG. 2. Relation of carbon soil removal properties of synthetic detergent formulations to the detergent concentration—tests made in distilled water at 140°F.

While the built and promoted formulations (A through F inclusive) exhibit a significant increase in carbon soil removal power as concentration is increased throughout the range studied, there is no important difference shown between the several formulations except at 0.15% concentration where the high Kreelon 4D products (A and D) are somewhat superior to the high builder formulations (B and E) and the high Carbose formulations (C and F).

The three unpromoted formulations display throughout the concentration series similar carbon soil removal properties although of a much lower order. One exception of small magnitude appears at 0.5% concentration. The high-soda ash formulation H is superior to the unbuilt synthetic K and the low-soda ash formulation G.

An important difference is shown between the Carbose-promoted formulations of Figures 2 and 3 and

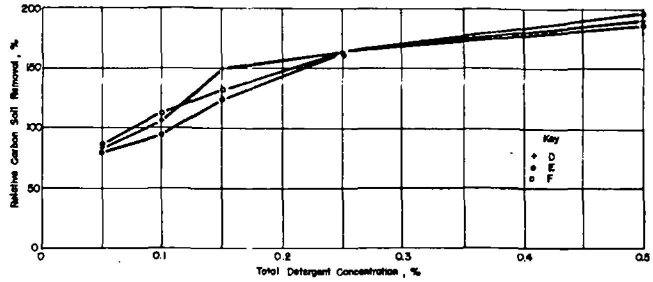

FIG. 3. Relation of carbon soil removal properties of synthetic detergent formulations to the detergent concentration—tests made in distilled water at 140°F.

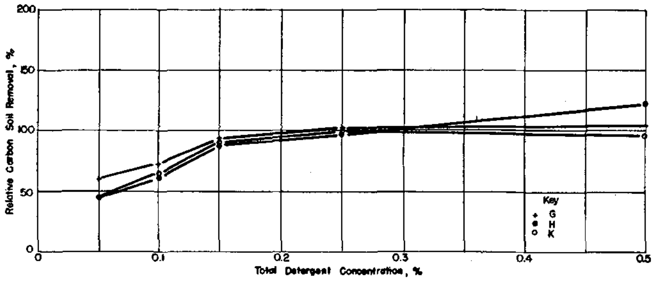

FIG. 4. Relation of carbon soil removal properties of synthetic detergent formulations to the detergent concentration—tests made in distilled water at 140°F.

the unpromoted formulations of Figure 4. The latter yield substantially flat curves beyond a concentration of 0.15%, that is the carbon soil removal power is independent of concentration and except when heavily built and used at high concentrations, does not exceed the soil removal power of the unbuilt synthetic detergent. On the other hand the Carbose-promoted formulations, while showing more rapidly increasing carbon soil removal power in the low concentrations than in the high, continue to give greater values up to the highest concentration tested, 0.5%, where relative carbon soil removal values approaching 200% are obtained.

Whiteness Retention as a Function of Detergent Concentration. The plots of whiteness retention versus detergent concentration corresponding to those previously presented for carbon soil removal are given in Figures 5 and 6 for the promoted and built synthetic detergents; and in Figure 7 for the unbuilt and soda ash-built synthetic detergent.

The complete independence of the two principal detergency factors—carbon soil removal and whiteness retention—is at once evident. The six promoted and built formulations, selected for equal soil removal properties under standard conditions, exhibit significantly different whiteness retention character-

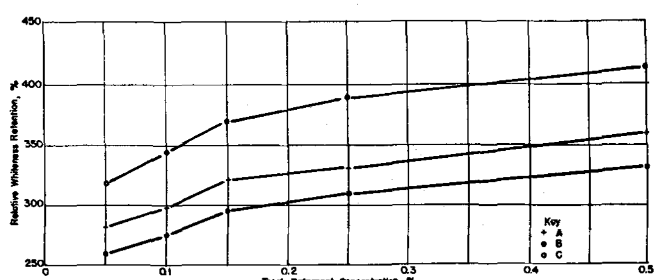

FIG. 5. Relation of whiteness retention properties of synthetic detergent formulations to the detergent concentration—tests made in distilled water at 140°F.

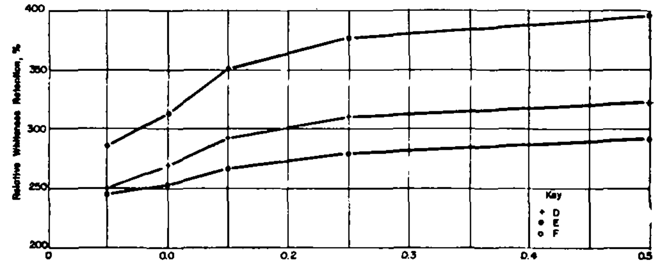

FIG. 6. Relation of whiteness retention properties of synthetic detergent formulations to the detergent concentration—tests made in distilled water at 140°F.

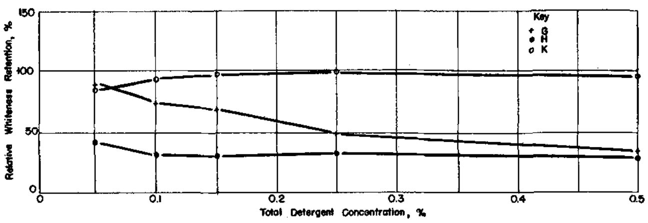

FIG. 7. Relation of whiteness retention properties of synthetic detergent formulations to the detergent concentration—tests made in distilled water at 140°F.

istics, these values showing, however, the common property of increasing with increasing detergent concentration. Similarly, the unbuilt and built synthetic detergent formulations display large differences in relative whiteness retention. Unlike the Carbose-promoted formulations, the unbuilt synthetic with respect to whiteness retention is practically independent of concentration; the low-soda ash-built formulation, G, yields whiteness retention values which decrease rapidly with increasing concentration; and the high-soda ash-built material, H, gives values which are independent of concentration and very low over the entire range.

The whiteness retention properties of the unpromoted formulations conform with general known laundry experience; the inorganic builders as a class exhibit poor whiteness retention as compared to both synthetic detergents and fatty acid soaps, and soda ash is one of the poorest in this respect. It approaches the novel however to find that the replacement of 15% of soda ash in Formulation H with an equal amount of Carbose (thus converting it to Formulation E) increases the relative whiteness retention at 0.25% total detergent concentration from 34% to 280%, and at 0.5% concentration, from 31% to 290%, an average increase of the order of 900%. The detergency-promoting characteristics of Carbose, though highly significant with respect to carbon soil removal, thus become most evident in whiteness retention measurements. The latter characteristic is so dominant that in our experience with detergent formulations containing any appreciable quantity of Carbose, the whiteness retention characteristics appear to be universally high and almost independent of the identity of the remaining components.

In laundering practice a given percentage increase in whiteness retention may not necessarily be considered of equal importance to a like increase in carbon soil removal. Above certain minimal values of the two factors necessary for acceptable performance under a given set of conditions, a modification of formulation yielding a given percentage increase in soil removal may often be more effective in terms of quality of work than the same percentage increase in relative whiteness retention, and depending upon conditions the converse may be true.

Detergency as a Function of Temperature in Built and Promoted Synthetic Detergent Systems

In commercial laundering a considerable latitude exists in washing temperatures. This may be attributed to personal preference, washing equipment design, variation in hot water supply and to the nature of the work being washed. These studies were made at temperatures of 100°F., 140°F., and 160°F., the extremes embracing most temperatures used in practice.

Carbon Soil Removal as a Function of Temperature. Carbon soil removal-temperature curves are plotted for the Carbose-promoted, modified soda-built systems in Figure 8; for Carbose-promoted, soda ash-built systems in Figure 9; and for the unpromoted formulations in Figure 10.

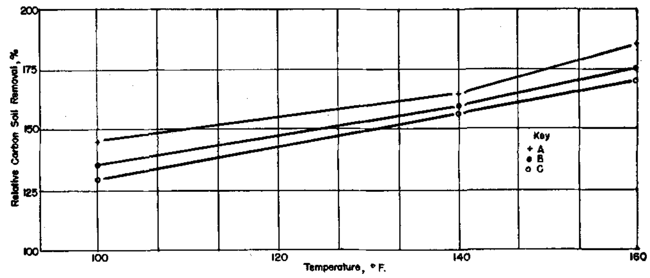

FIG. 8. Effect of temperature on the carbon soil removal properties of synthetic detergent formulations—detergent concentration 0.25%. Tests made in distilled water.

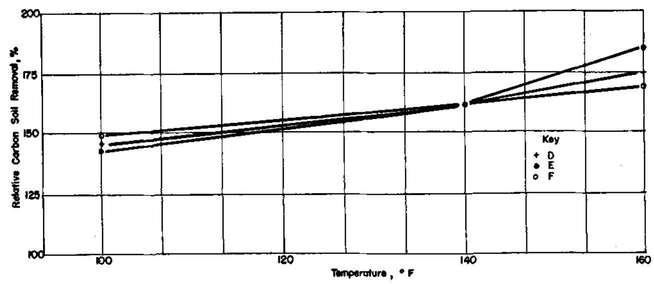

FIG. 9. Effect of temperature on the carbon soil removal properties of synthetic detergent formulations—detergent concentration 0.25%. Tests made in distilled water.

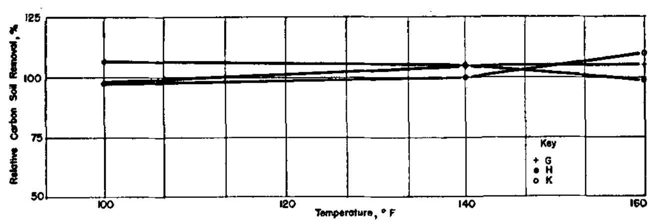

FIG. 10. Effect of temperature on the carbon soil removal properties of synthetic detergent formulations—detergent concentration 0.25%. Tests made in distilled water.

As was found true with reference to change in concentration, carbon soil removal values show little differential variation with change in temperature; that is, knowing the relation of carbon soil removal to temperature for one Carbose-promoted formulation, the performance of another such formulation having the same carbon soil removal at 140°F. can be predicted for other temperatures with moderate accuracy. The same rule holds for the unbuilt and built synthetic detergent formulation shown in Figure 10. The only significant exception is that of Formulation E, which contains a relatively large proportion of soda ash, at 160°F. The effectiveness of soda ash is increased at high temperature, and this property becomes apparent in this case where the detergent contains 50% of the material.

In addition to the fact that the Carbose-promoted products as a group yield higher carbon soil removal values at all temperatures than the unpromoted formulations, they also increase in carbon soil removal power with temperature whereas the unpromoted products are insensitive to large changes in temperature. Fatty acid soaps, as is well known, are sensitive to temperature and usually show a well-defined maximum carbon soil removal value within fairly narrow temperature limits. The promoted synthetic thus takes on this characteristic of soap but does not present a critical maximum in the working range of temperature investigated.

Whiteness Retention as a Function of Temperature. The whiteness retention-temperature curves corresponding to those presented for carbon soil removal are plotted in Figures 11 to 13 inclusive.

One characteristic is common to all formulations investigated in this study whether built or promoted

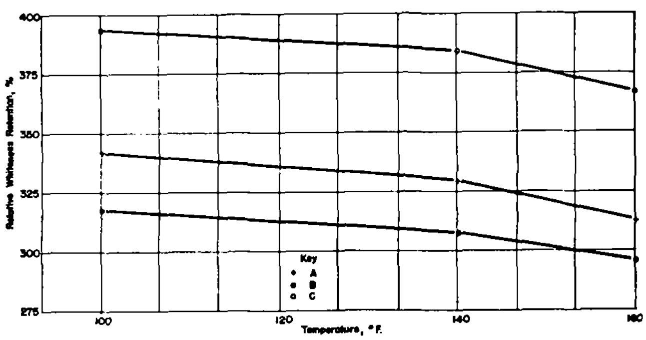

FIG. 11. Effect of temperature on the whiteness retention properties of synthetic detergent formulations—detergent concentration 0.25%. Tests made in distilled water.

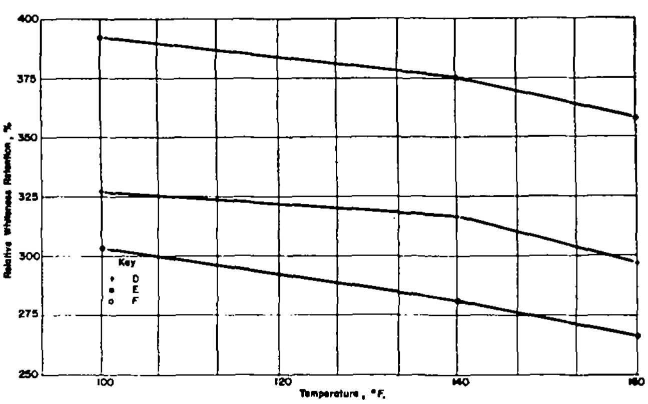

FIG. 12. Effect of temperature on the whiteness retention properties of synthetic detergent formulations—detergent concentration 0.25%. Tests made in distilled water.

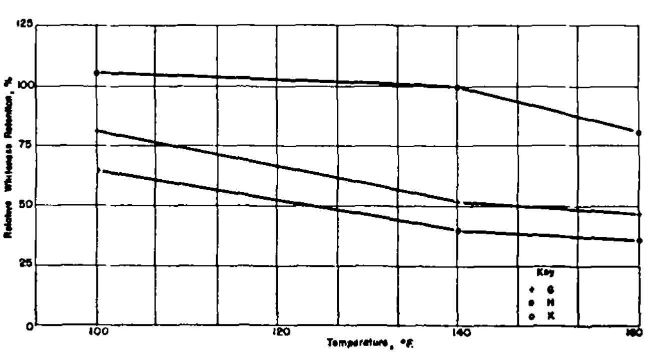

FIG. 13. Effect of temperature on the whiteness retention properties of synthetic detergent formulations—detergent concentration 0.25%. Tests made in distilled water.

—the whiteness retention varies inversely with the temperature. The rate of change is similar for all Carbose-promoted products but the whiteness retention remains, even at 160°F., at an effective level. At all temperatures, just as at all concentrations, whiteness retention remains largely a function of the quantity of promoter present.

The built formulations (G and H) show the usual loss in whiteness retention at all temperatures as compared to the synthetic detergent when tested alone. The latter exhibits little variation in whiteness retention with temperature change between 100°F. and 140°F. but is depreciated markedly at 160°F.

Conclusions

1. In detergent systems composed of various proportions of Kreelon 4D (sodium alkylaryl sulfonate), Carbose (sodium carboxymethyl cellulose), and inorganic builder (modified soda or soda ash), it has been shown that equal carbon soil removal power at standard conditions (0.25% detergent concentration in distilled water at 140°F.) connotes approximately equal carbon soil removal values for the different formulations at other temperatures from 100°F. to 160°F. and at other concentrations from 0.05% to 0.5%. The same is true of systems containing no Carbose and built or unbuilt.

2. With respect to both carbon soil removal and whiteness retention Carbose-promoted formulations yield higher values with increase in detergent concentration. In the case of unbuilt or soda ash-built Kreelon 4D formulations, carbon soil removal increases but whiteness retention remains constant or decreases with increase in concentration.

3. With increase in temperature, Carbose-promoted formulations yield increased carbon soil removal values but decreased whiteness retention. Unpromoted, built or unbuilt formulations are practically independent of temperature with respect to carbon soil removal and give decreasing whiteness retention values as the temperature is increased.

4. The partial substitution of alkali by Carbose in the formulations studied yields increases in detergency of large magnitude. This is typified in the comparison of Formulation H (Kreelon 4D 35%, soda ash 65%) and Formulation E (Kreelon 4D 35%, soda ash 50%, Carbose 15%). By this modification relative carbon soil removal values at 0.25% and 0.5% detergent concentration are increased approximately 67% and whiteness retention values approximately 900%.

5. The data presented emphasizes the individual importance and the independence of soil removal and whiteness retention values. Three formulations (D, E, and F), all yielding relative carbon soil removal values of 163% at 0.25% concentration and 140°F., gave relative whiteness retention values of 315, 280, and 374% respectively.

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