permit uninterrupted, unattended over-night operation. These may be listed as follows:

1. An apparatus designed for and heated with steam.
2. An improved air regulating system.
3. An improved air distributing system using a stainless steel manifold.
4. A safety valve is shown which eliminates the possibility of leaks in the water condensing system.
5. A different type of aeration tube assembly is described.

We are indebted to Mr. H. Flagler of the Research Engineering Department for the sketches inserted.

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The Effect of Sodium Carboxymethyl Cellulose on Synthetic Detergent Systems

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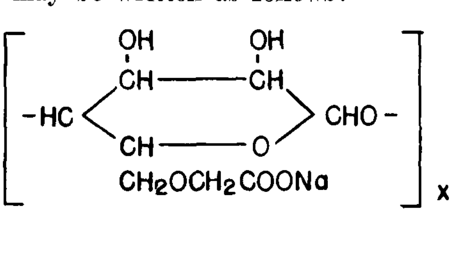
Introduction

FOLLOWING the termination of World War II in the European Theater, Hoyt, investigating certain phases of German industry, reported that certain forms of sodium carboxymethyl cellulose had been used in large quantities as a soap and synthetic detergent extender (1). Detailed information concerning its manufacture and properties and samples of one product, Tylose HBR, were sent to this country. At that time these laboratories held a contract with the Office of the Quartermaster General covering research on the development of laundering procedures and detergents suitable for use with sea water. In this connection Tylose HBR was evaluated for detergency promoting properties on three commercial synthetic detergents: "Arctic Syntex L," "Igepon T," and "Neutronyx 228," as hereinafter reported. Upon completing this sea water laundering investigation, attention was directed to the formulation and detergency evaluation of compositions based on a sodium alkyl aryl sulfonate type detergent and sodium carboxymethyl cellulose.

Although in this country sodium carboxymethyl cellulose is used in ice cream manufacture, textile finishing, paper sizing, and other equally diverse industries, its applicability to the field of detergency, judging from published information, appears relatively unknown. It is the purpose of this paper to present some new data on the effect of sodium carboxymethyl cellulose on the carbon soil removal and whiteness retention characteristics of several built and unbuilt synthetic surface active agents and to discuss effects of the material such as water softening properties which are of importance in the field of detergency.

Chemical Structure and General Properties of Sodium Carboxymethyl Cellulose

The chemical structure of sodium carboxymethyl cellulose may be written as follows:



In this idealized representation the glucose residue which forms the basic unit of the cellulose molecule is shown to be substituted in the primary hydroxyl group. The two secondary hydroxyl groups may similarly be substituted and the extent to which the cellulose is modified is expressed in terms of degree of substitution. If on the average one hydroxyl group in each glucose residue unit is substituted, this is termed one degree of substitution.

Sodium carboxymethyl cellulose in purified form is a white odorless and tasteless solid. It is believed to be physiologically inert (2). Its solubility in water varies with the degree of substitution; in general, the greater the degree of substitution, the greater the solubility. An extensive discussion of the chemistry of this material is given by Höppler (3), and a review covering properties, manufacture and uses, has been contributed by Hollabaugh *et al.* (4).

The Measurement of Detergency

In evaluating the effect of sodium carboxymethyl cellulose on synthetic detergent systems, our work largely has been confined to the experimental laundering of cotton fabrics. For satisfactory laundering such fabrics require highly effective detergents and therefore make excellent test material. It is our belief that detergency with reference to cottons may be considered in two phases. One—soil removal—applies to the capacity of a detergent solution to remove soil from a standardly soiled fabric; the other—whiteness retention—involves the capacity of the solution to suspend a colloidal soil and prevent its deposition upon an unsoiled standard fabric (5).

The laboratory methods used in determining the detergency data reported herein evaluate independently these two characteristics. They have not previously been published and accordingly are given in full in this section.

Pretreatment of Cotton Fabrics. Prior to use for detergency studies it is necessary to pretreat most cotton fabrics so as to remove the sizing or finish and to shrink the material.

In our work 14 pieces of a standard muslin[1] 36 in. x 54 in. are definished in a commercial monel metal wash wheel (24 in. x 34 in.) by the procedure indicated in Table I, using throughout water softened to below one

[1] Indian Head muslin (permanent finish) count 53 x 47, 5.15 oz. per sq. yd., manufactured by Nashua Mfg. Co., 40 Worth St., N. Y. 13, N. Y.

TABLE I

Pretreatment Procedure for Cotton Fabrics

Operation	Time	Temp.	Vol. of Water	Supplies
	min.	*°F.*	*liters*	
Break	30	180	40	100 g. NaOH
Rinse	5	180	80	none
Rinse	5	180	80	none
Suds	20	180	40	20 g. sodium stearate
Rinse	3	160	80	none
Rinse	3	140	80	none
Rinse	3	120	80	none
Rinse	3	100	80	none

grain $CaCO_3$ equivalent per gallon. Following the pretreating operation, the muslin load is extracted for 5 minutes and tumbled to dryness (15 minutes at 85° C.) in a commercial gas-heated laundry drier. This preheated cloth can be stored prior to soiling or may be used immediately.

Preparation of Standard Water-Bound Carbon Soiled Cloth. Thirty-five pieces of the definished standard muslin measuring approximately 10.5 x 36 in. are treated as follows:

Thirty-seven and three tenths liters of water softened to below one grain $CaCO_3$ equivalent per gallon are placed in a monel wash wheel (24 in. x 34 in.) and 441.2 grams of a commercial soluble oil[2] added to the water. The wheel is allowed to run 5 minutes in order to mix the water and the soluble oil, after which is added 306.3 grams of a carbon black dispersion[3] and the wheel again run for 5 minutes. The temperature during this step is held at 90°F.

The batch of cloth to be soiled is rapidly added piece by piece to the emulsion of carbon black and oil in the wash wheel. In order to impregnate the cloth thoroughly with the soil, the wheel is run at 32 r.p.m. for 30 minutes and stopped at 10-minute intervals while the cloth is untangled. The wash wheel speed is then reduced to 15 r.p.m., the dump valve opened and the carbon suspension allowed to drain off the cloth for a period of 30 minutes with the wheel running.

The cloth is removed piece by piece and passed once without folding through a power-driven household type wringer to squeeze out any residual aqueous dispersion. The pressure upon the wringer is adjusted to leave in the cloth soil solution equal to 120% ± 1% of the dry weight of the cloth.

When all the cloth has been passed through the wringer, it is placed in a commercial-type drier and tumbled without heat for 30 minutes at room temperature. This step prevents the migration of carbon or draining of the carbon suspension when the soiled cloth is hung on a line for final drying. The cloth pieces are removed and allowed to dry completely by hanging edgewise at room conditions for 48 hours.

After the above treatment the cloth is cut into test pieces measuring 2½ in. ± 1/32 in. by 3½ in. ± 1/32 in. using a guillotine paper cutter.

Upon the completion of each batch of standard soil it is necessary to determine whether it meets certain specifications in regard to carbon load and tenacity. The cloth is tested by means of a standard detergent[4] using the procedure given for the carbon soil removal evaluation of synthetic detergents. The soil is evaluated in distilled water against the standard detergent over the range of concentrations indicated in Table II. For the soil to be accepted it is necessary that the number of milligrams of carbon removed per liter fall within the range indicated for each concentration.

TABLE II

Tenacity Range of Acceptable Soil

Concentration, %	Range in Mgs. of Carbon per Liter
0.05	3.7- 4.8
0.1	4.4- 6.0
0.2	9.3-11.9
0.25	10.3-12.4
0.3	11.3-13.5
0.5	11.3-13.3

Carbon Soil Removal Evaluation of Synthetic Detergents. To evaluate the soil removing characteristics of synthetic detergents, a standard Launder-O-Meter[5] is used for washing the test pieces and a Fisher Electrophotometer,[6] without filter, for determining the light absorption of the detergent solution before and after washing. The preferred method of expressing soil removal results for an unknown detergent requires individual determinations of soil removal value of the unknown and of a standard detergent sample, the results being expressed in terms of percentage of type detergent.

The test procedure is as follows:

A 0.25% solution of the material under test is prepared in distilled water. One hundred milliliters of this solution are added to each of ten one-pint Launder-O-Meter jars. The jars are allowed to stand in a constant temperature bath until the temperature of the detergent solution rises to 140°F. ± 2°, at which temperature the tests are conducted. Fifteen stainless steel balls (¼-in. diameter) are placed in each jar, after which two pieces of the standard soiled cloth measuring 2½ x 3½ in. are added to each of nine of the jars. In the tenth jar are placed two pieces of unsoiled but pretreated white Indian Head muslin of the same size. (This jar is used later to determine the blank turbidity of the detergent solution.)

Immediately following the addition of the cloth swatches, the jars are sealed and placed in the Launder-O-Meter. The Launder-O-Meter is started and allowed to run for 10 minutes at a speed of 42 ± 1 r.p.m. The jars are removed from the Launder-O-Meter and immediately replaced in the constant temperature bath. The jar containing the unsoiled cloth is held separate from the rest. The contents of each jar containing soil suspension are poured through a coarse screen which retains the balls and the soiled swatches into a large beaker which stands in the constant temperature bath. The composite suspension thus obtained is mixed thoroughly and a sample placed in a 10-mm. light absorption cell. Using the Fisher Electrophotometer, the light absorption is obtained with as short a delay as possible. This value is referred to as the "Suspension Value." The light absorption value of the tenth jar is determined in a similar manner and is known as the "Blank." The light absorption values thus obtained are not a linear function of the weight of carbon removed. In order

[2] Shell Virgo 38-P obtainable from the Shell Oil Company, 154 Bagley St., Detroit 26, Mich.

[3] Colloidal Black Dispersion No. 10, an aqueous carbon dispersion manufactured by Binney and Smith Co., 41 E. 42nd St., N. Y., N. Y.

[4] The standard detergent used by this laboratory is Kreelon 4D.

[5] Type L2Q-EF-SPA, manufactured by Atlas Electric Devices Company, 361 West Superior St., Chicago, Illinois.

[6] Model 7-089, manufactured by Fischer Scientific Company, Pittsburgh, Pa.

TABLE III

Analytically Determined Composition of Sodium Carboxymethyl Cellulose Products

	Tylose HBR	Carbose
	%	%
Sodium Carboxymethyl Cellulose	32.9	50.8
Na_2CO_3	9.5	12.0
$NaHCO_3$	12.7	0.0
NaCl	14.0	15.7
H_2O	32.2	10.6
Undetermined	......	10.9*

* Believed to be primarily sodium monochloracetate and sodium glycolate.

to convert light absorption values to milligrams of carbon removed per liter of detergent solution, a calibration curve for the Fisher Electrophotometer must be constructed by obtaining the light absorption values of suspensions prepared by adding various amounts of carbon black dispersion to distilled water[7] (0 to 36 mg. of carbon per liter being the range of interest when using a 10-mm. light absorption cell). The light absorption values are plotted versus the concentration of carbon in milligrams per liter on rectangular coordinate graph paper in order to obtain a standard calibration curve.

Calculations. The "Suspension Value" and the "Blank" obtained as described above are converted by means of the calibration curve to milligrams of carbon per liter of solution. The soil removal value sought is obtained by taking the difference between the converted values.

The preferred method of reporting soil removal values requires the use of a standard detergent as a reference or control material. All "mgs. of carbon per liter of solution" values for detergent materials are then expressed in terms of "Percentage of Type" by dividing the milligrams of carbon value of the test material by the milligrams of carbon value for the standard or control material which is determined concurrently on the same stock of standard soil and multiplying by 100. (This compensates for day to day variation in the standard soil used.)

Whiteness Retention Evaluation of Synthetic Detergents. Standard pretreated muslin is ironed with a 36-inch single roll household electric ironer set at 328-338°F. to remove wrinkles. After ironing, the cloth is cut into pieces measuring $2\frac{1}{2}$ in. $\pm$ $\frac{1}{32}$ in. x $3\frac{1}{2}$ in. $\pm$ $\frac{1}{32}$ in. The light reflectance of each side of every piece of cloth is measured by means of a Hunter Multi-purpose Reflectometer[8] using the green filter, and a standard white backing, having a reflectance of 78.2% based on the reflectance of MgO being equal to 100%, behind the cloth. The two reflectance values for each test piece are mentally averaged and the piece placed in the proper compartment of a multi-compartmented box, marked off in 0.1% units. In using the swatches, to simplify calculations, the swatches for any single test are drawn from any one compartment.

A 0.2625% solution of the detergent to be tested is prepared in distilled water and 100-ml. portions added to each of five Launder-O-Meter jars. Into each of these is pipetted a 5-ml. sample of a standard soil solution prepared by diluting 40.0 grams of carbon black dispersion to a liter with distilled water.[9] The solution is shaken vigorously each time immediately before the sample is taken. Fifteen steel balls are placed in each jar, after which the jars are brought to 140°F. in a constant temperature water bath, then placed in the Launder-O-Meter and rotated for five minutes. The Launder-O-Meter is stopped, the jars are removed, and two pieces of the standard cloth described above are placed in each jar. The jars are replaced and rotated for 15 minutes. The cloths are removed, rinsed by dipping singly in three one-liter beakers of distilled water, the water being renewed for each set of 10 cloths. The cloths are then ironed by passing three times through the ironer set at a temperature of 328-338°F. The reflectances of both sides of each piece are measured using the Hunter Reflectometer as before described. The reflectances of the 10 pieces of cloth are averaged and the whiteness retention value for the detergent under test calculated, this value being equal to the ratio of the average reflectance after washing to the original reflectance, multiplied by 100.

Precision of Detergency Tests. In a series of 13 replicate carbon soil removal tests of one Kreelon 4D-Tylose HBR formulation in which the results were expressed relative to a standard detergent tested at the same time, the average relative carbon soil removal was found to be 160.0% with an average deviation of $\pm$ 4.9% or an actual average percentage deviation of $\pm$ 3.1%. These replicate tests were made by three operators on 9 soil batches over a period of 18 months.

A series of 12 replicate whiteness retention tests of a synthetic detergent gave an average value of 53.6% $\pm$ 0.94% or an actual average percentage deviation of $\pm$ 1.8%. These tests were carried out by three operators over a period of 12 months.

These relatively high degrees of precision may uniformly be attained, but only through careful attention to technique, and in the case of the carbon soil removal test especially through the use of a standard comparative detergent to minimize the effect of temperature, humidity, and aging upon the soil.

Test Materials

The analyses and other identifying characteristics of the principal detergents, alkaline salts and sodium carboxymethyl cellulose products 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%.

Sodium Metasilicate—A commercial grade having the following characteristics: Alkalinity to methyl orange as Na_2O—29.5%; SiO_2—28.5%; Insolubles—<0.05%; CO_2 as Na_2CO_3—<1.0%.

Yellow Hoop[10]—A special type of modified soda with an average Na_2CO_3-$NaHCO_3$ ratio of 1:1.39 by weight.

"Silicated Ash"[11]—A reaction product of sodium silicate and soda ash, containing unreacted sodium carbonate and a silicate probably in the form of a

[7] It has been determined experimentally that the addition of detergents to the standardization solutions produces no effect on the light absorbing properties of the carbon.

[8] Manufactured by Henry A. Gardner Laboratory, Inc., Apparatus Division, 4723 Elm Street, Bethesda 14, Maryland.

[9] Because of temporary unavailability of Colloidal Black Dispersion No. 10, Aqua Black B, another product of Binney and Smith Co., was used in the present whiteness retention work, 28.55 grams of the latter replacing 40.0 grams of the former.

[10] Produced by Wyandotte Chemicals Corporation, Wyandotte, Michigan.

[11] Produced by Wyandotte Chemicals Corporation, Wyandotte, Michigan.

glass since no crystalline silicate is disclosed when examined by X-ray diffraction. A typical analysis of this product is as follows: Na_2O—45%; Na_2CO_3—68.5%; SiO_2—8.9%; H_2O—15.0%.

Carbose C-1716A[12]—One of several technical forms of sodium carboxymethyl cellulose. Its analysis, as well as that of Tylose HBR, is given in Table III. In most of the work reported in this paper, Carbose C-1716A (referred to hereafter simply as "Carbose") was used. Further development has yielded products having sensibly greater detergency promoting properties. Therefore 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 in no way to indicate maximum detergency promotion which it is possible to obtain.

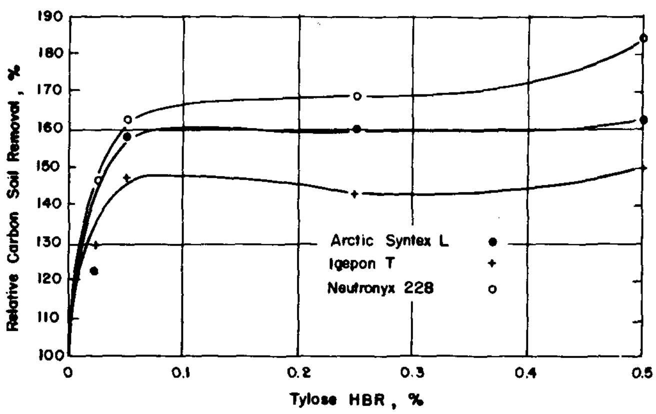


FIG. 1. Effect of Tylose HBR on carbon soil removal characteristics of synthetic detergents.

Detergent concentration 0.5%. Diluted synthetic sea water ($CaCO_3$ equiv. 7 gr./gal.). Temperature 140°F. pH 8.8.

Kreelon 4D[13]—A sodium alkyl aryl sulfonate type of synthetic detergent having the following approximate composition: Organic sulfonate — 40%; inorganic salts—60%.

Effect of Sodium Carboxymethyl Cellulose on Synthetic Detergents in Sea Water. Because of the interest of the Office of the Quartermaster General in finding an effective salt water detergent, the first extensive tests of Tylose HBR were made in conjunction with various types of synthetic detergents in synthetic sea water[14] diluted with distilled water to a hardness equivalent to 7 gr. $CaCO_3$ per gallon.

In Figure 1 and Figure 2 are shown, respectively, the relative carbon soil removal and whiteness retention results obtained from mixtures of Tylose HBR with three commercial synthetic detergents: Arctic Syntex L,[15] the sodium salt of a sulfated monoglyceride; Igepon T,[16] the sodium salt of a fatty acid sulfonated amide; and Neutronyx 228,[17] a polyalkyl ether condensate of fatty acids.

All values for each detergent are expressed relative to a value of 100% for the detergent alone; therefore, the relative increase in effectiveness of the detergents

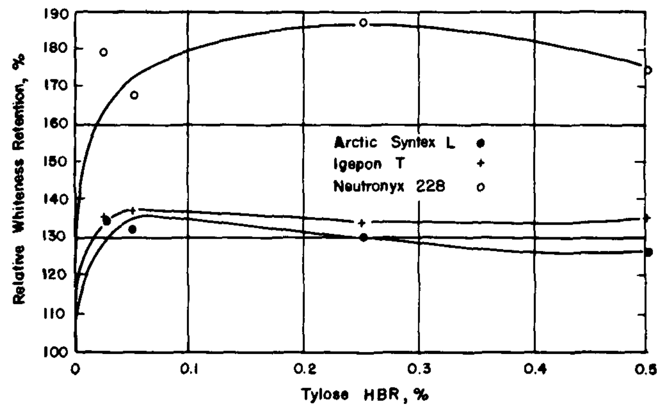


FIG. 2. Effect of Tylose HBR on whiteness retention characteristics of synthetic detergents.

Detergent concentration 0.5%. Diluted synthetic sea water ($CaCO_3$ equiv. 7 gr./gal.). Temperature 140°F. pH 8.8.

associated with the addition of Tylose HBR may be compared but not the detergencies of the various systems.

In every case both carbon soil removal and whiteness retention properties were greatly improved, with the nonionic detergent Neutronyx 228 showing the greatest relative improvement.

In most cases substantially the maximum effect was reached with relatively small amounts of Tylose HBR, approximately 10% based on the weight of the synthetic detergent being a practical level.

Comparison of Detergency-Promoting Properties of Sodium Carboxymethyl Cellulose Products

Upon confirming the detergency-promoting properties of sodium carboxymethyl cellulose, work was immediately begun upon the development of processes for the manufacture of this material. This work was carried through the pilot plant stage and resulted in a technical form of sodium carboxymethyl cellulose, bearing the trade name Carbose and characterized in a previous section.

A comparison of the effectiveness of Carbose and Tylose HBR in increasing the carbon soil removal properties of Kreelon 4D is shown in Figure 3. Various amounts of the sodium carboxymethyl cellulose products were added to 0.25% solutions of Kreelon 4D in distilled water and the carbon soil removal values determined at 140°F.

Over the range of concentrations tested the two materials showed similar properties with Carbose being slightly superior to Tylose HBR except at the highest level, 10% based on the weight of Kreelon 4D.

The remainder of the work reported here has been done using Carbose. Because sodium carboxymethyl cellulose products cannot be considered as pure compounds, but differ in detergency-promoting characteristics as well as in other properties, depending on the nature of the raw material and the variables of the manufacturing process, the results obtained cannot necessarily be extended to other products. A large number of samples of sodium carboxymethyl cellulose of both domestic and foreign origin have been examined in these laboratories and without exception the materials have exhibited the property of promoting the detergency of synthetics. The degree or range of promotion has been found, however, to be different for different samples as would be expected.

[12] Produced by Wyandotte Chemicals Corporation, Wyandotte, Michigan.

[13] Produced by Wyandotte Chemicals Corporation, Wyandotte, Michigan.

[14] Synthetic Sea Water (6)

$MgCl_2 \cdot 6H_2O$	11.0 g.
$CaCl_2 \cdot 2H_2O$	1.6 g.
Na_2SO_4	4.0 g.
NaCl	25.0 g.

Dissolve in distilled water and dilute to 1 liter.

[15] Colgate-Palmolive-Peet Co., Jersey City, New Jersey.

[16] General Dyestuff Corporation, New York City.

[17] Onyx Oil and Chemical Company, Jersey City, New Jersey.

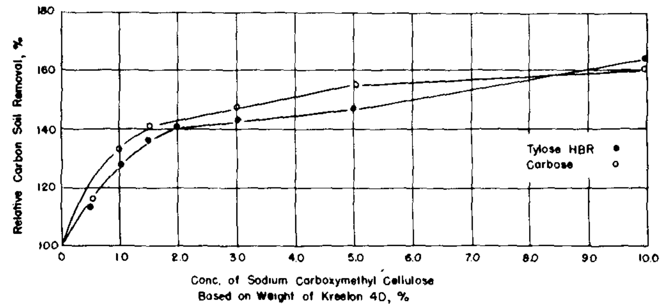


FIG. 3. Comparative effect of sodium carboxymethyl cellulose products on the carbon soil removal characteristics of Kreelon 4D in 0.25% concentration at 140°F. in distilled water.

Detergency in the Systems Kreelon 4D-Carbose-Alkaline Salts

The carbon soil removal and whiteness retention characteristics of systems containing Kreelon 4D, Carbose and various alkaline salts were investigated in some detail. Two simple salts—sodium carbonate and sodium metasilicate—and two complex commercial products—Yellow Hoop and "Silicated Ash"—all suitable for use as detergent "builders," were included in these tests. Tests were conducted, according to the standard methods previously described, in distilled water at 140°F. All data was calculated relative to the standard detergent, Kreelon 4D=100%.

In obtaining this data, 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%. This approach permits the construction of triangular coordinate graphs on which can be plotted detergency values for any three-component systems and this in turn makes possible the rapid visual summation and interpretation of a large mass of data.

To permit of the easiest comparison, individual datum points have been omitted and the graphs bear only iso-detergency lines at various levels. By the use of these graphs there immediately may be located any number of combinations of detergent, promoter, and builder, which have certain desired characteristics.

Carbon Soil Remoal Data. Results of the carbon soil removal tests upon the four systems are presented in Figures 4-7 inclusive. The four sets of curves exhibit several general correspondences. Most of the contour lines open on the Kreelon 4D-Carbose axis and show a marked distortion toward the point representing builder = 100%. The area of greater carbon soil removal usually is within the bounds approximated by Kreelon 4D = 50-80%, Carbose = 20-50%, builder = 0-30%.

Under the conditions of these tests, a good grade of unbuilt soap of a type commonly used in commercial laundering, has a relative carbon soil removal value of 147%. Along the 150%-contour line, an infinite number of mixtures are found which approximately equal this value, yet which may contain as little as 12% of synthetic detergent (see Figure 6). Mixtures represented by all points falling within the area bounded by the 150%-contour line and the Kreelon 4D-axis exceed, in varying degree, this soap in carbon soil removing capacity.

The carbon soil removal properties of formulations having a constant ratio but varying absolute quantities of two components with an inversely varying quantity of the third component are found along a straight line drawn from the point representing 100% of the third component to the desired point on the opposite side of the triangle. For example, in Figure 4, all formulations containing Yellow Hoop and Kreelon 4D in a 1:1 ratio with the quantity of Car-

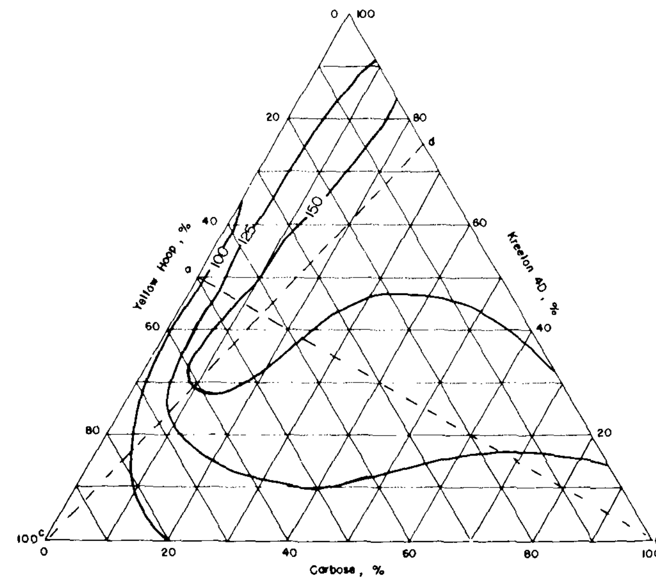


FIG. 4. Carbon soil removal characteristics in the System Kreelon 4D-Carbose-Yellow Hoop.

Total concentration 0.25%. Distilled water at 140°F. All values based on Kreelon 4D = 100% when tested under the same conditions.

bose varying from 0 to 100% are found on the dashed line, *ab*. Similarly line *cd* represents the loci of all formulations containing Kreelon 4D and Carbose in a 3:1 ratio with the quantity of Yellow Hoop varying from 0 to 100%.

It is notable in all four graphs that a fundamental difference exists in the trend of carbon soil removal values obtained when the quantity of either Kreelon 4D or Carbose is varied as compared to that obtained when the quantity of any one of the builders is varied.

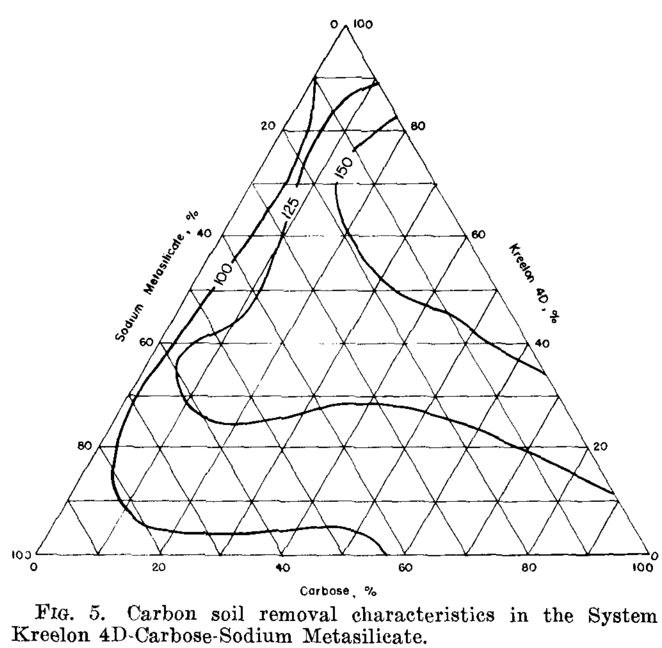


FIG. 5. Carbon soil removal characteristics in the System Kreelon 4D-Carbose-Sodium Metasilicate.

Total concentration 0.25%. Distilled water at 140°F. All values based on Kreelon 4D = 100% when tested under the same conditions.

In Figure 4 there is seen to be a distinct maximum in the carbon soil removal when the percentage of Carbose is varied from 0 to 100% (line *ab*), the maximum occurring approximately at the point Carbose

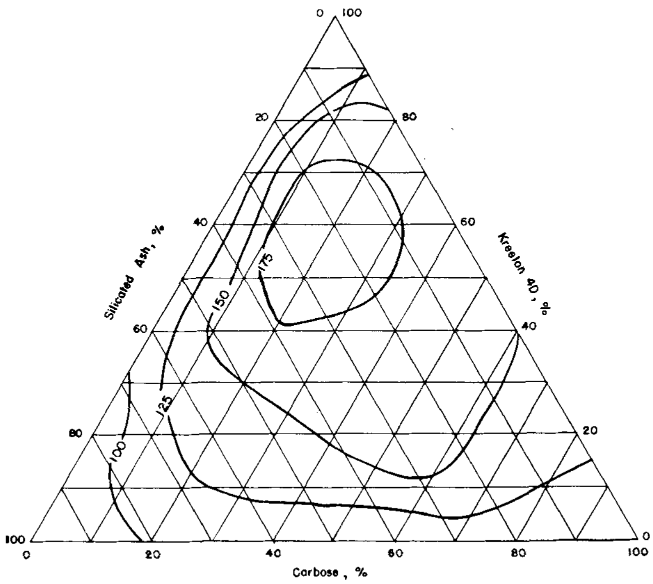


FIG. 6. Carbon soil removal characteristics in the System Kreelon 4D-Carbose-Silicated Ash.

Total concentration 0.25%. Distilled water at 140°F. All values based on Kreelon 4D = 100% when tested under the same conditions.

= 15%. In contrast, it may be observed that increasing the quantity of builder, in this case Yellow Hoop, from 0 to 100% (line *cd*) makes it possible to *maintain* a given level of detergency as the total quantity of Kreelon 4D and Carbose is reduced but no marked maximum is obtained. These facts are more clearly expressed in Figure 8 which shows the shape of the carbon soil removal curves taken along the lines *ab* and *cd*.

In general, if a constant total concentration and a

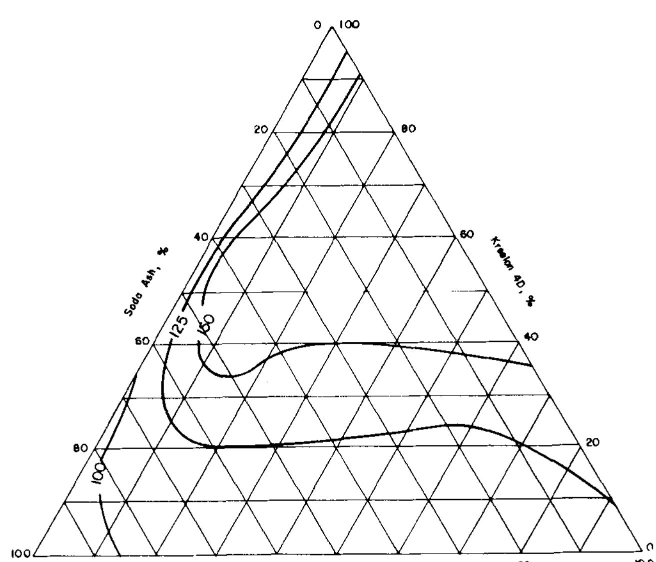


FIG. 7. Carbon soil removal characteristics in the System Kreelon 4D-Carbose-Soda Ash.

Total concentration 0.25%. Distilled water at 140°F. All values based on Kreelon 4D = 100% when tested under the same conditions.

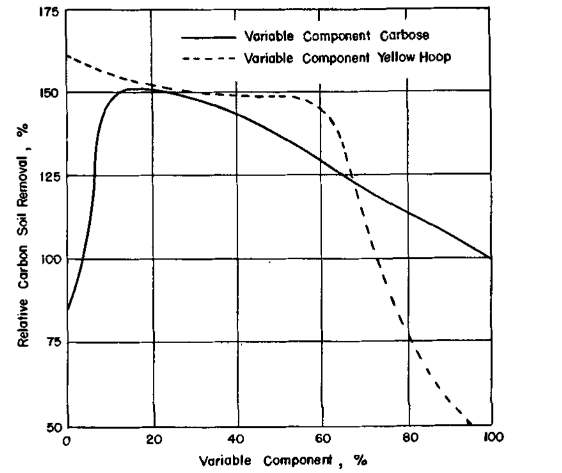


FIG. 8. Relative effect on carbon soil removal of the addition of Yellow Hoop to a Kreelon 4D-Carbose System and of Carbose to a Kreelon 4D-Yellow Hoop System.

Total concentration 0.25%. Distilled water at 140°F. All values based on Kreelon 4D = 100% when tested under the same conditions.

constant ratio of either Kreelon 4D to builder or Carbose to builder are maintained, then upon increasing the quantity of the Carbose or Kreelon 4D, the carbon soil removal values go through a maximum. But when the builder is the variable component, increasing its

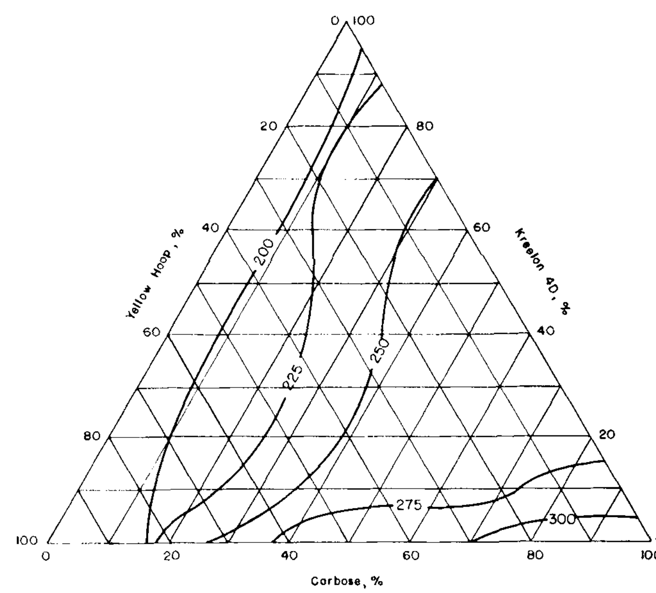


FIG. 9. Whiteness retention characteristics in the System Kreelon 4D-Carbose-Yellow Hoop.

Total concentration 0.25%. Distilled water at 140°F. All values based on Kreelon 4D = 100% when tested under the same conditions.

concentration results in the maintenance of a given level of carbon soil removal as the total concentration of Kreelon 4D and Carbose decreases over a considerable range. In other words, carbon soil removal properties of a Kreelon 4D-Builder may be sensibly increased by the replacement of part of each by Carbose. On the other hand, the replacement of part of either component in a Kreelon 4D-Carbose formulation by builder will not increase to a large degree the detergency but will maintain it at substantially the same level as considerable amounts of synthetic detergent and promoter are replaced by the builder.

Whiteness Retention Data. In Figures 9-12 inclusive are presented the results of the whiteness retention tests made on the four systems. The effect of Carbose on whiteness retention is shown to be very great and largely independent of the composition of the rest of the system. That is, for the systems investigated, the whiteness retention properties inherent in Carbose are such as to make negligible the contribution to whiteness retention of the builders and of the synthetic detergent. Thus in Figure 10, it is apparent that the whiteness retention characteristic of a composition consisting of 10% Carbose and 90% sodium metasilicate are approximately identical with those of one containing 10% Carbose and 90% Kreelon 4D. Further, although the effects of the different alkaline salts upon carbon soil removal vary sensibly, the difference in the effects upon whiteness retention in the presence of Carbose is slight. This is demonstrated by the fact that the contour lines of the respective graphs bear a strong similarity to each other.

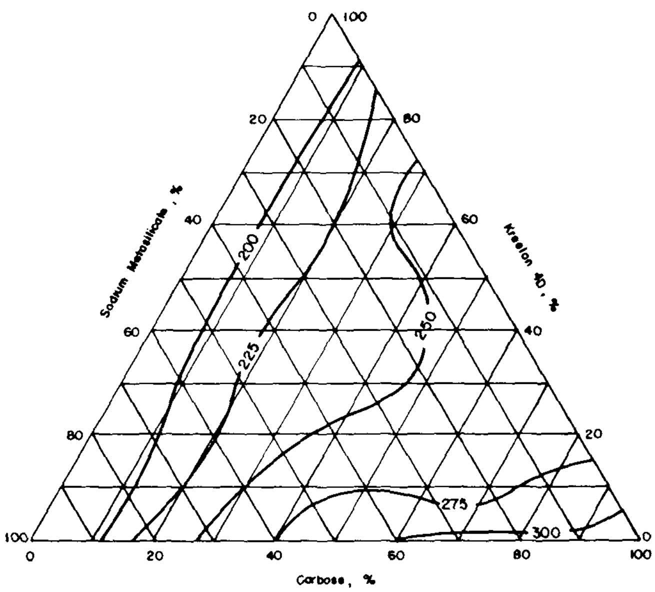


FIG. 10. Whiteness retention characteristics in the System Kreelon 4D-Carbose-Sodium Metasilicate.

Total concentration 0.25%. Distilled water at 140°F. All values based on Kreelon 4D = 100% when tested under the same conditions.

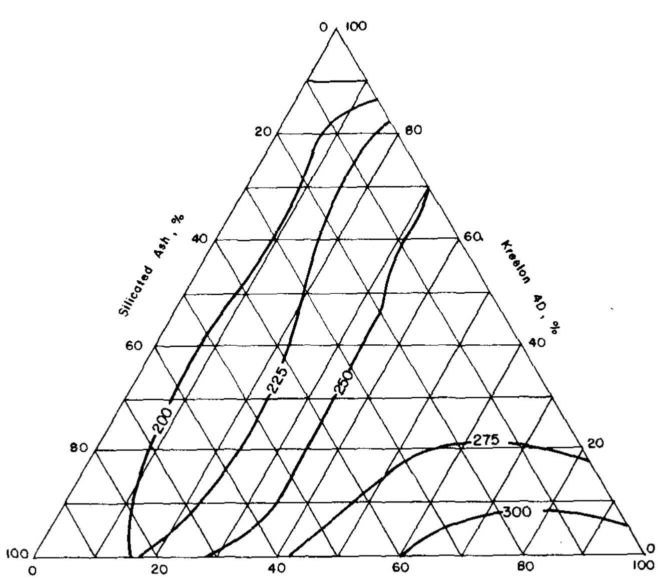


FIG. 11. Whiteness retention characteristics in the System Kreelon 4D-Carbose-Silicated Ash.

Total concentration 0.25%. Distilled water at 140°F. All values based on Kreelon 4D = 100% when tested under the same conditions.

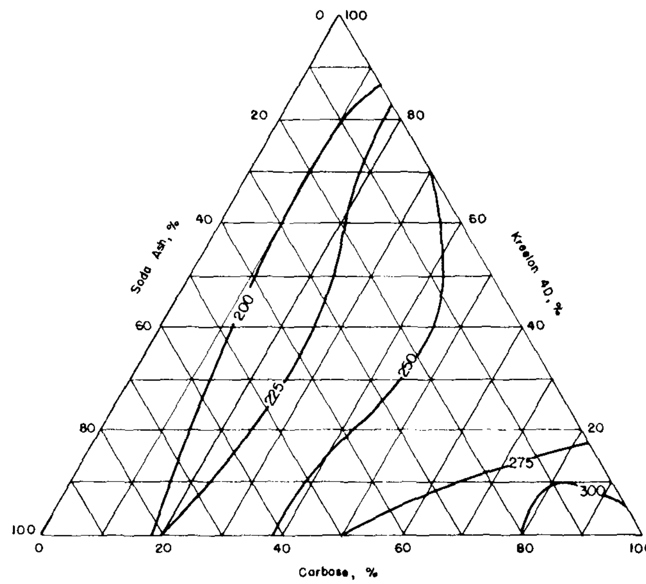


FIG. 12. Whiteness retention characteristics in the System Kreelon 4D-Carbose-Soda Ash.

Total concentration 0.25%. Distilled water at 140°F. All values based on Kreelon 4D = 100% when tested under the same conditions.

In order to point out the significance of the effect of Carbose upon whiteness retention it may be mentioned that based on a value of 100% for Kreelon 4D, the various alkaline salts tested yield values ranging around 15% and the high grade unbuilt laundry soap previously mentioned, a value of 197%. In general the addition of 10% Carbose to almost all combinations of Kreelon 4D and any one of the four alkaline salts included in this work will result in products having whiteness retention characteristics equal to or greater than a typical high grade unbuilt soap.

Water Softening Properties of Sodium Carboxymethyl Cellulose

Although the water softening properties of sodium carboxymethyl cellulose are less significant than the detergent promoting characteristics previously described, the sequestering effect upon hard water cations is appreciable.

In Figure 13 the water softening properties of Carbose and tetrasodium pyrophosphate, a commonly used polyphosphate-type softener, are illustrated in terms of the number of milliliters of 0.261% sodium oleate solution required to produce a stable foam in 50 mls. of a synthetic hard water[18] of 8.4 gr. per gallon.

In this test increasing the concentration of Carbose beyond 0.2% results in little decrease in soap demand; however, at this point the soap requirement to produce sudsing is reduced by approximately 35%.

This water softening property or protective capacity against the effects of hard water is further shown in Figures 14 and 15. Carbon oil removal and whiteness retention values are shown for Kreelon 4D in

0.25% concentration with various amounts of Carbose at 140°F. in distilled, and synthetic hard waters[18] of 8.4 and 15.0 grs. per gallon.

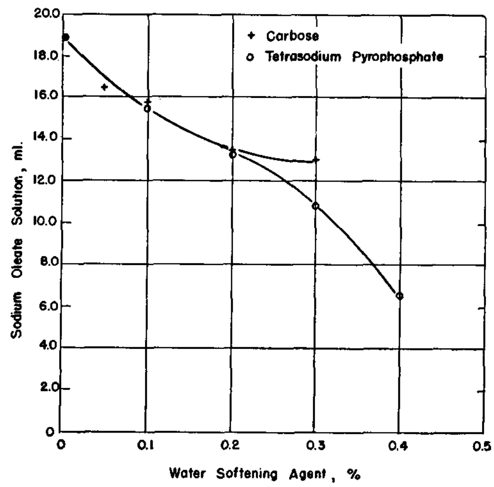


FIG. 13. Water softening properties of Carbose. Water 8.4 gr. $CaCO_3$ equiv./gal. Temperature 150°F.

Although it is commonly supposed that anionic synthetic detergents are not depreciated when used in hard water, this supposition is only partially correct. As illustrated in Figure 14, the carbon soil removal properties are definitely impaired. The degree of improvement is much less than in the case of fatty acid soaps and, of course, the reaction products of the anionic synthetic detergent and the hard water salts are soluble, but in all cases investigated in these laboratories some depreciation does occur. It is also evident that in spite of the normal deleterious effect of hard water upon the synthetic detergent, the addition of as little as 10% Carbose makes it possible to obtain greater carbon soil removal in 15 gr. water than is possible in distilled water in which no Carbose is used.

In Figure 15 the effect of hard water in conjunction with a synthetic anionic detergent is shown to be favorable with respect to whiteness retention characteristics. As would be expected, the addition of Carbose results in material improvement of whiteness retention in both distilled and hard waters. The cause of this favorable effect is unknown but may be due to a possible superior soil suspending action of the calcium or magnesium salts of the alkyl aryl sulfonate as compared to that of the sodium salt.

This water softening effect has been observed in the field where the descaling of laundry washing equipment frequently has occurred upon changing from conventional detergent formulations to ones containing Carbose and no other sequestering agents.

Summary

Certain forms of sodium carboxymethyl cellulose have been shown to be highly effective as synthetic detergent promoters. Formulations containing a sodium alkyl aryl sulfonate type of synthetic detergent, alkaline salts and a type of sodium carboxymethyl cellulose developed for high detergency promoting properties surpass high quality fatty acid soaps in both carbon soil removal and whiteness retention on cottons.

[18] Prepared by dissolving the proper quantities of calcium chloride and magnesium sulfate in distilled water to give a mol ratio of Ca:Mg of 2:1 and the desired hardness both expressed as $CaCO_3$ equivalent.

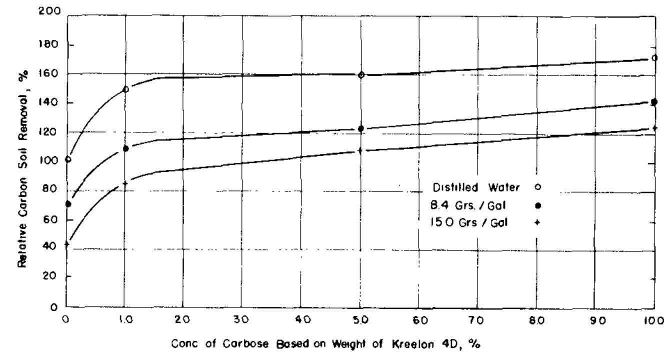


FIG. 14. Effect of the addition of Carbose on the carbon soil removal characteristics of Kreelon 4D in 0.25% concentration at 140°F. in distilled and hard waters.

Ternary diagrams have been presented for systems containing Kreelon 4D, a sodium alkyl aryl sulfonate type of detergent; Carbose, a commercial detergent grade of sodium carboxymethyl cellulose; and each of four alkaline salts. From these diagrams can be selected visually an infinite number of formulations having any desired level of detergency within the range covered and which will meet other requirements such as maximum or minimum foaming, high or low alkaline salt content, etc.

Sodium carboxymethyl cellulose promotes detergency in both hard water and diluted synthetic sea water and in fact has actual water softening properties, being able to sequester or otherwise reduce the effect of hard water cations. A sodium alkyl aryl sulfonate type of detergent combined with the proper proportions of sodium carboxymethyl cellulose in as high as 15 gr. water exhibits detergent properties superior to those of the synthetic detergent alone in distilled water.

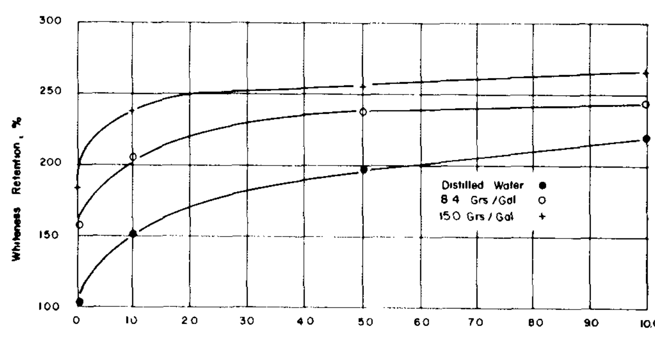


FIG. 15. Effect of the addition of Carbose on the whiteness retention characteristics of Kreelon 4D in 0.25% concentration at 140°F. in distilled and hard waters.

Methods having a relatively high order of precision for the evaluation of detergency have been presented in detail. By these methods two fundamental characteristics of detergency — carbon soil removal and whiteness retention— as applied to the laundering of cotton fabrics may be independently measured.

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