

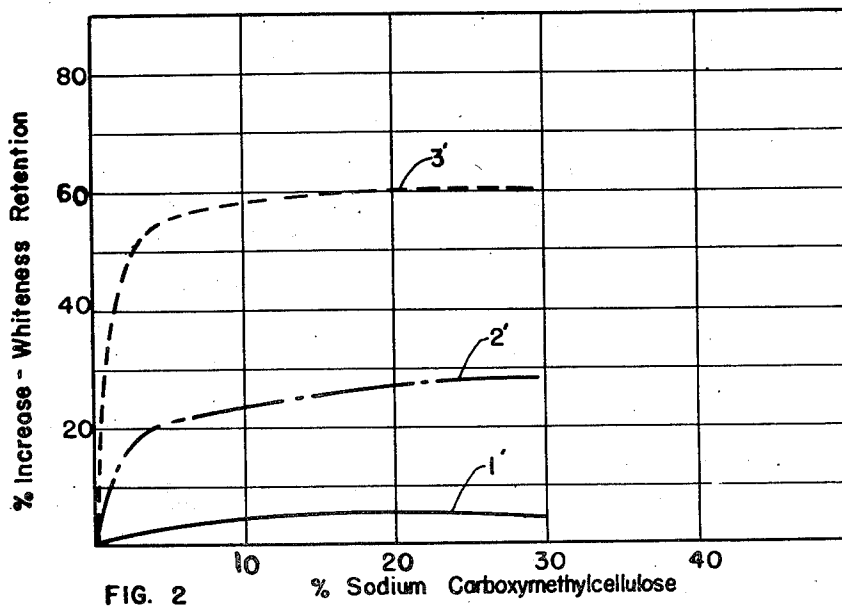
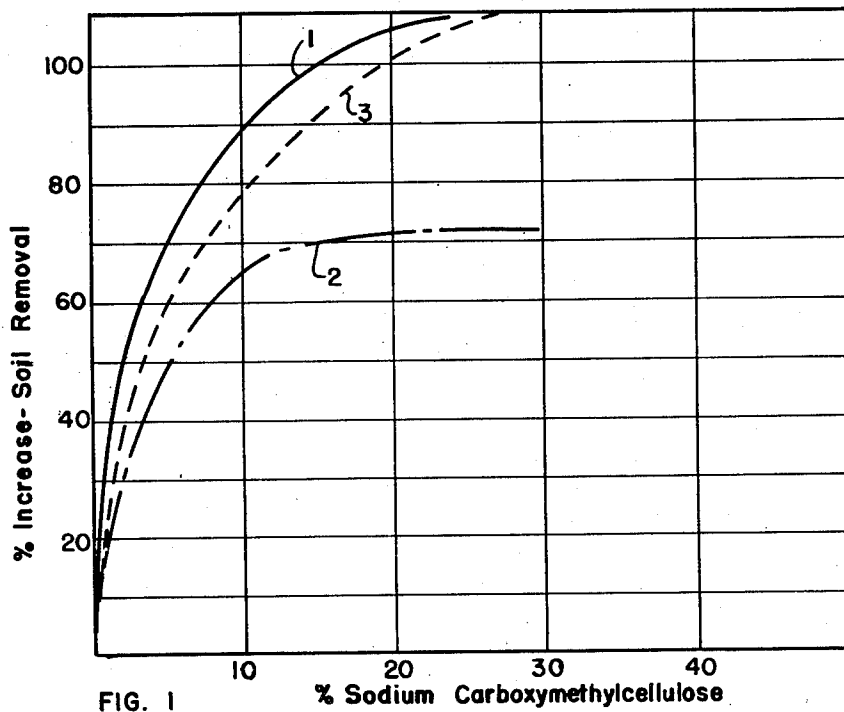
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METHOD OF MAKING A SYNTHETIC DETERGENT COMPOSITION

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METHOD OF MAKING A SYNTHETIC
DETERGENT COMPOSITION

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1 Claim. (Cl. 252—161)

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The present invention relates to a synthetic detergent composition containing an organic compound additive agent, whereby the detergency and cleaning power of such composition when placed in solution and used in the usual manner for washing fabrics and the like, results in a remarkable increase in detergency.

We have discovered that a synthetic detergent of the alkyl aryl sulfonate type, and derived from a petroleum hydrocarbon fraction and an aromatic hydrocarbon of the benzene series, such as disclosed in Guenther U. S. Patent No. 2,220,099, together with as low as 1% and up to equal parts by weight of a water-soluble salt of cellulose glycollic acid (e. g. ¹sodium carboxymethylcellulose and higher alkyl homologues thereof), has the ability of increasing from 40 to over 100% the detergent powers when compared to the alkyl aryl sulfonate alone. Alkyl aryl sulfonates of this type, such as sodium "keryl" benzene sulfonate are commercially available in a form containing about 40% by weight of the alkyl aryl sulfonate and 60% of sodium sulfate, the larger portion of the latter being inherently present in the product as a result of the process of making it wherein the alkyl aryl sulfonic acid-sulfuric acid mixture is neutralized with caustic soda. Our invention is primarily designed to be applicable to the alkyl aryl sulfonate in such commercially available form; however, it is equally well operable with the alkyl aryl sulfonate in its "salt-free" form, i. e. in the absence of the sodium sulfate.

Much effort has heretofore been expended in the objective of improving the detergent power of the alkyl aryl sulfonate type of detergents. Various inorganic compounds such as phosphates, borates, chlorides, acetates, carbonates and the like, have been added for such purposes. Likewise, organic compounds such as amines, and quaternary ammonium compounds have been tried. However, none of these prior attempts have resulted in the greatly increased effectiveness shown by the composition of our invention.

The composition of our invention also displays the most unexpected property of maintaining its increased detergency, and in some instances producing even greater improvement in detergent properties, where the hardness of the water in

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which the composition is dissolved is increased.

We have also discovered a novel method of incorporating the ingredients of our composition whereby the rate of water solubility thereof is increased to approximately tenfold of that of an ordinary, simple mechanical admixture of the ingredients.

We have also found that the presence of inorganic alkaline salts, such as those used as "soap-builders" (e. g. sodium carbonate, -bicarbonate, modified soda, trisodium phosphate, sodium metasilicate) is not only compatible with the composition of our invention, but it also imparts a noticeable improvement in detergency over and above that already achieved by the alkyl aryl sulfonate-carboxymethylcellulose combination. Such alkaline salts are suitably added in the amount of $\frac{1}{16}$ to equal parts by weight of the alkyl aryl sulfonate product present.

To the accomplishment of the foregoing and related ends and to enable any person skilled in the art readily to understand and practice the invention, the following full and concise description and annexed drawing set forth the best mode in which we have contemplated applying the principle thereof.

In said annexed drawing:

Fig. 1 is a chart showing the relationship between the percentage content of sodium carboxymethylcellulose to the percentage increase in detergency when measured by the carbon soil removal test procedure herein subsequently described in greater detail; and

Fig. 2 is a chart showing similar relationships to that of the chart of Fig. 1 and based upon detergent properties determined by the whiteness retention test procedure subsequently herein described in greater detail.

As previously indicated, the alkyl aryl sulfonate ingredient of the composition of our invention, is suitably derived from a process involving the condensation of a petroleum hydrocarbon fraction having a boiling point in the range of 150-300° C., with an aromatic hydrocarbon of the benzene series, such as benzene, toluene, xylene, etc.; followed by the sulfonation of such condensation product to form alkyl aryl sulfonic acids which are subsequently neutralized, such as by means of caustic soda, to form the water-soluble alkyl aryl sulfonates. During such neutralization step, excess sulfuric acid present in the alkyl aryl sulfonic acid mixture is neutralized to an inorganic salt, such as sodium sulfate.

The latter is customarily, and in a commercial

¹"Cellulose glycollic acid" and "carboxymethylcellulose" are alternative forms of nomenclature for the same chemical compound, being so referred to in the prior literature and patents. The basic synthesis of same is disclosed in British Patent No. 138,116 wherein monochloroacetic acid and its homologues are reacted with alkali cellulose.

alkyl aryl sulfonate detergent product, permitted to remain and in some instances might even be increased by external addition. A proportion of about 60% sodium sulfate is usually found to be present in commercially available alkyl aryl sulfonate type of synthetic detergents. Whether pure (i. e. sulfate-free) alkyl aryl sulfonate or the "built" (Na_2SO_4 -containing) type is employed, the improved results of the composition of our invention are equally well obtained. The terms "alkyl aryl sulfonate" and "sodium keryl benzene sulfonate" when generally or more broadly employed hereinafter, in both the description and claims, shall be regarded as including both the sulfate-free and sulfate-containing forms of this ingredient of our compositions. Specific identification will of course be made of the respective forms where conciseness or particularization so requires.

The other essential ingredient of the composition of our invention is a water-soluble salt of cellulose glycollic acid. Such a salt should contain 0.3 to 1.0 mol glycollic acid residue per glucose unit of cellulose. Sodium carboxymethylcellulose is an example of such a water-soluble salt of cellulose glycollic acid. Other alkali metal and basic nitrogen salts of cellulose glycollic acid may be employed, however the sodium salt is the one which is most economically and commercially suitable.

The sodium carboxymethylcellulose may be simply admixed in dry, fine particle form with the dry, solid alkyl aryl sulfonate; or it may be first dissolved in a water solution, along with the alkyl aryl sulfonate, and such solution subsequently dried or dehydrated to solid form, such as in the form of a flake where the solution is subjected to the action of a drum drier, or in the form of minute, substantially globular particles, where the solution is spray dried. The resultant composition comprising the essential ingredients of the alkyl aryl sulfonate and the water-soluble salt of cellulose glycollic acid, when dissolved in water solution in a concentration range of 0.03 to 1.0%, produces an increase in detergency which, according to standard methods of measurement, has been found to be at least 40% greater than that of the alkyl aryl sulfonate alone.

The increased detergent efficiency of the composition of our invention has been determined by the following described tests which are relatively rigorous and severe, being designed to measure not only the ability of the detergent composition to remove dirt and soil, but to keep it in solution and to prevent redeposition onto the surface of the article being washed.

Soil removal test procedure

A standard soiled cloth is made by treating a piece of cloth with a standard suspension of carbon black. Pieces of such treated cloth are placed in "Launder-O-Meter" jars containing the detergent solution to be tested. The jars are then placed in a "Launder-O-Meter" test washing machine and rotated for a given period of time, at a constant temperature. Thereafter a sample of the detergent solution is placed in the light absorption cell of a Fisher electrophotometer and the light absorption value of such solution then obtained. By use of a calibration curve, the milligrams of carbon taken up by the detergent solution, or removed from the pieces of test cloth, is then determined as a function of the light absorption reading. Thus, the value of the milligrams

of carbon per liter of detergent solution constitutes a measure of the amount of carbon soil removed from the standard soiled cloth and thus the higher value of the milligrams of carbon per liter of solution obtained in this carbon soil removal test, the greater the detergent properties of the solution tested.

A series of detergent compositions consisting of sodium "keryl" benzene sulfonate (having a 58% by weight Na_2SO_4 content) alone with varying added amounts of sodium carboxymethylcellulose incorporated therein by means of drying a water solution of the ingredients, were subjected to soil removal tests, with the following tabulated results:

TABLE I

[Tests conducted at 140° F., in distilled water, 8.4 grain and 30 grain per gallon hard waters.]

Proportion of NaCMC ¹ to alkylaryl sulfonate ²	Per cent by weight conc. of alkyl aryl sulfonate in detergent solution	Per cent by weight conc. of NaCMC in detergent solution	Mgs. of carbon removed per liter of solution		
			Distilled water	8.4 ³ Grain water	30 ³ Grain water
1:80	0.25	0.003	9.3	9.3	7.5
1:40	0.25	0.0062	13.3	12.8	10.7
1:20	0.25	0.0125	14.4	12.4	11.5
1:10	0.25	0.025	15.7	14.7	10.9
1:5	0.25	0.05	16.9	16.1	12.3
1:2.5	0.25	0.10	19.0	15.3	14.1
			19.3	15.9	15.9

¹ Sodium carboxymethylcellulose.

² Sodium "keryl" benzene sulfonate, 58% Na_2SO_4 content.

³ Hardness calculated as CaCO_3 ; mol ratio of Ca^{++} to Mg^{++} , 2 to 1.

In Fig. 1, the per cent increase of the soil removal values obtained from the compositions containing sodium carboxymethylcellulose, as compared to the composition not containing it, is graphically represented in the form of curves. Thus, curve 1 shows the percentage increase in soil removal detergency, according to the per cent of sodium carboxymethylcellulose present (total solids basis), for the tests conducted in distilled water; curve 2 for 8.4 grain hard water and curve 3 for 30 grain hard water. It will be seen, that as low as 1% by weight of sodium carboxymethylcellulose on the basis of the total solids present in the detergent solutions, results in over a 40% increase in the carbon soil removal detergent properties; and that even where the hardness of the water in which the detergent compositions are used is increased, such detergency increase still maintains. In other words, curves 2 and 3 are not materially distinctive in characteristics from curve 1. It will also be noted from Table I and from Fig. 1, that the increase in detergency is rapidly achieved when only relatively small amounts (i. e. as little as 1%) of the sodium carboxymethylcellulose are present. The curves tend to level off; or their slope approaches zero, in the range of 15 to 30% sodium carboxymethylcellulose. Hence, a percentage range of 1 to 30% by weight of sodium carboxymethylcellulose on the basis of the alkyl aryl sulfonate ingredient present, represents the most suitable operative range.

Whiteness retention test procedure

A description of this test procedure is as follows:

A standard carbon suspension is prepared consisting of a carbon black dispersion in water, the latter being distilled or hard water of desired hardness. This standard carbon suspension is then placed in "Launder-O-Meter" jars to which

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has previously been added uniform quantities of the detergent solution to be tested. Pieces of standard white cloth are also put in the jars and the latter are placed in the "Launder-O-Meter" test machine for given periods of rotation at constant temperature. After this, the jars are removed from the "Launder-O-Meter," the pieces of cloth removed and rinsed free of loosely held carbon. The pieces of cloth are then ironed dry and light reflectance values are taken of each piece of cloth. The percentage difference of such final reflectance value from the original light reflectance value of the original standard white cloth gives the final test reading in terms of percentage of whiteness retention.

The same detergent solutions as subjected to the previously described soil carbon removal test, were subjected to this whiteness retention test procedure, with the following tabulated results:

TABLE II

Proportion of NaCMC ¹ to alkyl aryl sulfonate ²	Per cent by weight conc. of alkyl aryl sulfonate in detergent solution	Per cent by weight conc. of NaCMC in detergent solution	Per Cent Whiteness Retention		
			Distilled water	8.4 Grain water	30 Grain water
-----	0.25	-----	68.1	62.4	45.9
1:80	0.25	0.003	68.9	71.5	69.0
1:40	0.25	0.0062	69.4	73.8	67.2
1:20	0.25	0.0125	72.9	73.5	69.5
1:10	0.25	0.025	74.0	76.6	69.9
1:5	0.25	0.05	72.5	76.2	72.1
1:2.5	0.25	0.10	72.2	79.9	73.7

¹ Sodium carboxymethylcellulose.

² Sodium "keryl" benzene sulfonate, 58% Na₂SO₄ content.

³ Hardness calculated as CaCO₃; mol ratio of Ca⁺⁺ to Mg⁺⁺, 2 to 1.

In Fig. 2, the per cent increase in the foregoing whiteness retention values of the alkyl aryl sulfonate-sodium carboxymethylcellulose compositions as compared to those for the alkyl aryl sulfonate alone, are graphically shown in the form of the curves 1', 2' and 3'. Each of these curves corresponds to the values obtained for distilled water, 8.4 grain hardwater and 30 grain hardwater, respectively. The remarkable deduction to be made from these results is that the whiteness retention properties increase greatly in proportion to the degree of water hardness, contrary to normal expectations. And it will be seen from the values given in Table II that the per cent whiteness retention for 30 grain hardwater are substantially equal to those for distilled water, even though the alkyl aryl sulfonate solutions without the sodium carboxymethylcellulose present show a considerable drop in whiteness retention values when going from the distilled to 30 grain water.

Further observing curves 1', 2' and 3' of Fig. 2, it will be seen that the per cent increase improvement in deterative performance as measured by the whiteness retention test occurs rapidly with a relatively small amount (1%) of sodium carboxymethylcellulose present, and that the maximum percentage increase is reached at about 15 to 30%. These curves confirm the observation made in connection with those of Fig. 1, namely: that 1 to 30% by weight of sodium carboxymethylcellulose on the basis of total solids present demarks the most suitable operative range content.

When the alkyl aryl sulfonate ingredient is employed in its pure or salt-free form, equivalent improvement in the detergent properties are obtained. Solutions of salt-free sodium "keryl"

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benzene sulfonate, with and without the addition of sodium carboxymethylcellulose, were made up in concentrations of 0.25% and 0.0875%, the latter percentage corresponding to the actual alkyl aryl sulfonate or active agent content of a Na₂SO₄-containing solution of 0.25% sodium "keryl" benzene sulfonate, viz: $0.25 \times 35\% = 0.0875\%$. These solutions were then subjected to the carbon soil removal detergency tests previously described and the following results were obtained:

TABLE III

Conc. of salt-free sodium "keryl" benzene sulfonate	Conc. of NaCMC ¹	Mgs. of carbon removed per liter of solution distilled water	Per Cent Increase for NaCMC ¹ addition
0.25	0.0	10.9	-----
0.25	0.025	16.7	53
0.0875	0.0	10.0	-----
0.0875	0.025	16.9	69

¹ Sodium carboxymethylcellulose.

It will thus be seen that the addition of the sodium carboxymethylcellulose to the Na₂SO₄-free form of alkyl aryl sulfonate produces an improvement in detergency increase equivalent to that obtained where the Na₂SO₄-containing product is employed.

We have also discovered a novel process for making the composition of our invention, the advantages of which are to be found in the unusual improvement in the rate of the solubility of the resultant product. This process comprises the steps of first dissolving the cellulose glycollic acid salt or the sodium carboxymethylcellulose in water in approximately a 1 to 10% solution; then adding the alkyl aryl sulfonate ingredient (in either sulfate-free or -containing form) in an amount sufficient to produce a 10-50% total solids content of the resultant mixture, agitating and heating to effect improved solution, dispersion or suspension; and finally drying the aqueous mixture to solid form by passing it through a drum drier or a spray drier. The following is a more specific example of the practice of the improved process for making the composition of our invention:

Sodium carboxymethylcellulose in the amount of 80 grams were dissolved in 500 cc. of distilled water with vigorous agitation resulting in a viscous solution. Distilled water in the amount of 220 cc. were then added to this solution, whereupon 200 grams of sodium "keryl" benzene sulfonate (58% Na₂SO₄ content) was added to the solution. This represented a proportion of 80 grams to 200 grams or 1 to 2½ parts by weight of sodium carboxymethylcellulose to sodium "keryl" benzene sulfonate, present in the mixture. This mixture was then stirred and heated to 90° C. and was then passed through a heated drum drier, producing a dried flaked product which was subsequently ground to a particle size of 40 mesh or finer. The product of the last stated example, as well as similarly made products having different proportions of sodium carboxymethylcellulose, but made in the same manner, were then subjected to the following solubility-rate test:

The dry, solid compositions after being passed through a 40 mesh screen, were dissolved in the amount of 0.5 gram at room temperature in 500 milliliters of distilled water contained in a 600 milliliter beaker, being stirred until dissolved.

The time required for effecting such dissolution

was then noted. Simple mechanical mixtures of the same proportions of the solid ingredients were also made and subjected to the same solubility rate test. The individual sodium "keryl" benzene sulfonate-Na₂SO₄ and sodium carboxymethylcellulose ingredients were also tested for their rate of solubility. The results were tabulated as follows:

TABLE IV

Ratio: NaCMC ¹ to sodium "keryl" benzene sulfonate ²	Percentage NaCMC ¹ (Total Solids Basis)	Dissolution Time	
		Mechan- ical Mixture	Dried Solution Mixture
----	----	Seconds	Seconds
----	100	³ 30	30
1:80	1.23	270	30
1:40	2.4	270	32-34
1:20	4.76	285	30
1:10	9.1	300	30
1:5	16.67	330	30
1:2.5	28.6	360	150

¹ Sodium carboxymethylcellulose.
² 58% Na₂SO₄ content.
³ 18 min.

It will thus be seen that the solubility rate of the compositions of our invention, made by our above described process, essentially involving the initial solution of the ingredients and subsequent drying thereof, results in an increase of 2 to 10 times the rate of solubility as compared to a simple mechanical admixture of the same ingredients in the ordinary dry, solid form.

Our above described process for initially combining the alkyl aryl sulfonate and sodium carboxymethylcellulose ingredients in the form of their aqueous solutions, is also eminently well adapted for incorporation in the commercial manufacture of alkyl aryl sulfonates where such latter chemical compounds are necessarily prepared in the form of aqueous solutions prior to drying to a solid form. The addition of a sodium carboxymethylcellulose aqueous solution to the alkyl aryl sulfonate solution at such stage in the commercial manufacture of the latter presents a convenient and economic procedure for merging our novel method for making our composition with the process for making one of its essential ingredients.

Where inorganic alkaline salts, which are customarily used as alkaline builders for soaps, are employed, even a still better improvement in detergency is obtained in the compositions of our invention. Such addition of inorganic alkaline salts are preferably made in the amount of as low as 1/16 to several parts by weight per each part of the alkyl aryl sulfonate ingredient present, and include such compounds as sodium carbonate, -bicarbonate, modified soda, trisodium phosphate and sodium metasilicate. Carbon soil removal tests, in distilled water, were performed upon compositions of our invention containing representative additions of such inorganic alkaline salts. The tested compositions were formulated upon the basis of 10 parts (by weight) of alkyl aryl sulfonate, 1 part of sodium carboxymethylcellulose and 4 parts of alkaline salt. The results obtained were as follows:

TABLE V

Conc. of Additive Agent (Per cent by weight in 0.25% Na K. B. S. ² solution)				Mgs. of carbon removed per liter of solution (distilled water)
Na CMC ¹	Sodium carbonate	Trisodium phosphate	Sodium metasilicate	
0.025	-----	-----	-----	9.3
0.025	0.1	-----	-----	16.9
0.025	-----	0.1	-----	17.5
0.025	-----	-----	0.1	19.0
0.025	-----	-----	0.1	17.7

¹ Sodium carboxymethylcellulose.
² Sodium "keryl" benzene sulfonate (58% Na₂SO₄).

It will thus be seen that the detergent compositions of our invention are not only compatible with relative highly alkaline detergent solution additive agents, but that such additive agents impart a slightly cumulative improvement in detergent properties.

It may be noted the carboxymethylcellulose ingredient of our compositions need not be of any specific grade of refinement in order to achieve the desired results, but can vary over a range of grades of purity—from a comparatively crude, technical grade which might contain unreacted cellulose, to a grade of maximum purity.

Other modes of applying the principle of our invention, in addition to the one hereinabove described and illustrated in detail, may be employed, provided the structural elements stated by the following claim or the equivalent of such elements be utilized.

We, therefore, particularly point out and distinctly claim as our invention and discovery:

The method of making a synthetic detergent composition comprising the steps of preparing a 1-10% by weight water solution of sodium carboxymethylcellulose, adding sodium alkyl benzene sulfonate, whose alkyl group is derived from a petroleum hydrocarbon fraction boiling in the range of 150-300° C., thereto in the proportion of 2.5-100 parts to 1 part by weight, solids basis, of said sodium carboxymethylcellulose, heating the resultant mixture to approximately 90° C. and agitating, and then drying the resultant solution to solid form.

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