March 11, 1952 J. E. HANSON 2,589,190

DETERGENT COMPOSITION

Filed July 29, 1947 2 SHEETS—SHEET 1

DETERGENCY VS. CARBOXYL CONTENT OF ADDITIVE

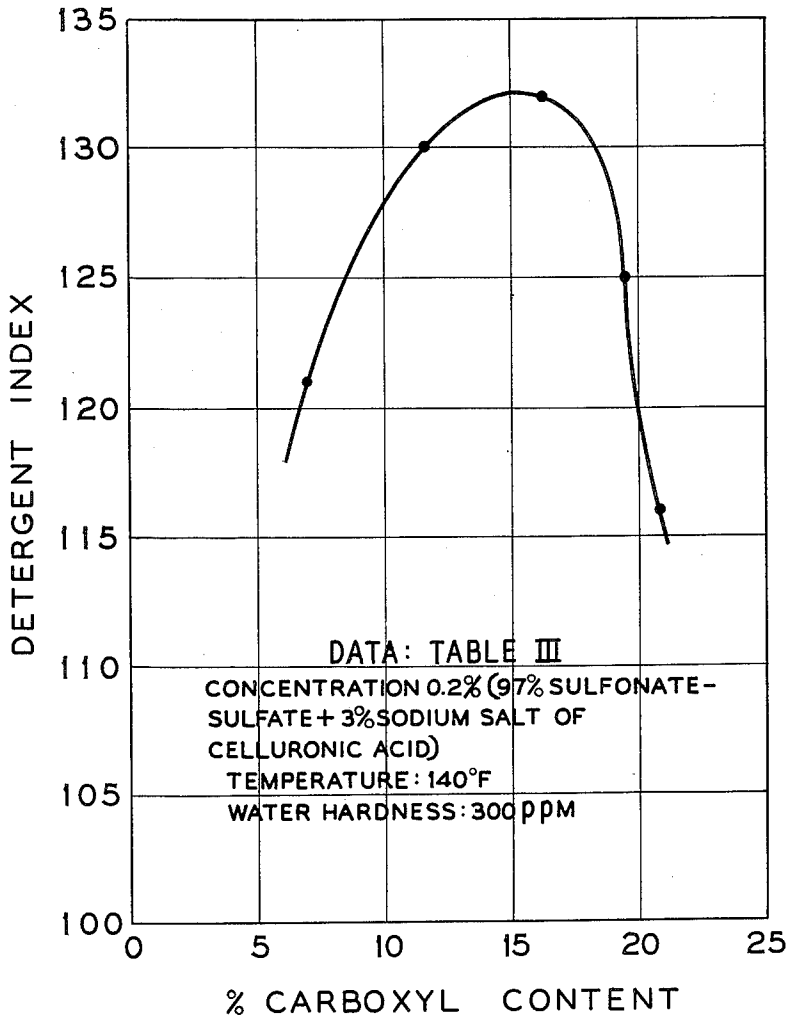

FIG. 1

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March 11, 1952 J. E. HANSON 2,589,190

DETERGENT COMPOSITION

Filed July 29, 1947 2 SHEETS—SHEET 2

EFFECT OF ADDITIVE'S CONCENTRATION ON DETERGENCY

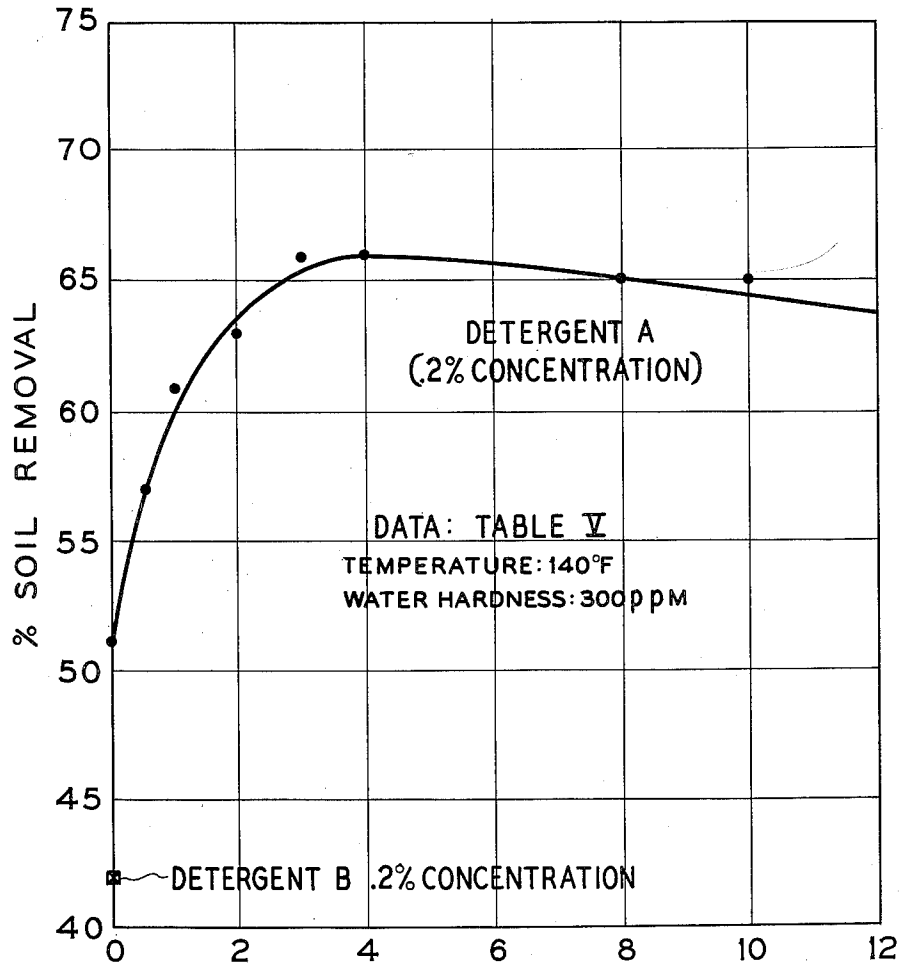

FIG. 2

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UNITED STATES PATENT OFFICE

2,589,190

DETERGENT COMPOSITION

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7 Claims. (Cl. 252—161)

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This invention relates to improved detergent compositions and more particularly to anionic and non-ionic detergent compositions containing small amounts of a celluronic acid salt of a monovalent cation, capable of enhancing the detergent characteristics of said compositions. Specifically it relates to the alkaryl sulfonate-type detergent compositions containing small amounts of a celluronic acid salt of a monovalent cation.

The term "celluronic acid" as used in this specification designates the product of selective and controlled oxidation of cellulose wherein only the primary hydroxyl group of anhydroglucose units in the cellulose molecule has undergone oxidation to a carboxyl group, as will be explained hereinafter.

According to the present invention, a remarkable and unexpected improvement of the detergent properties is secured by intimately incorporating, as by dispersing or dissolving, a celluronic acid salt of a monovalent cation in a composition containing a soap or a synthetic detergent. It has been found that a much greater degree of soil removal is secured in various washing operations because of the presence of such celluronic acid salt additive in the detergent composition than is otherwise obtainable in the absence of said additive. A remarkable feature of the detergent compositions improved in accordance with the present invention is the small amount of the celluronic acid salt required to effect a significant improvement of detergency.

The aforementioned salts of celluronic acids responsible for the new and significant improvement of detergency are prepared by the reaction of an aqueous solution of a base, e. g., sodium hydroxide, pyridine, ammonia, upon the particular derivatives of cellulose produced by the oxidation of cellulose fibers with nitrogen dioxide (NO_2—N_2O_4) gases.

The oxidized celluloses obtained in this oxidation are known under the name of celluronic acids and in contradistinction to other types of oxidized celluloses, are the products of a selective and controlled oxidation of cellulose. Through the application of particular oxidation techniques, as disclosed, for instance, in U. S. Patent No. 2,232,990 to Yackel et al., only the primary hydroxyl in each anhydroglucose unit of the cellulose molecule is converted to a carboxyl group

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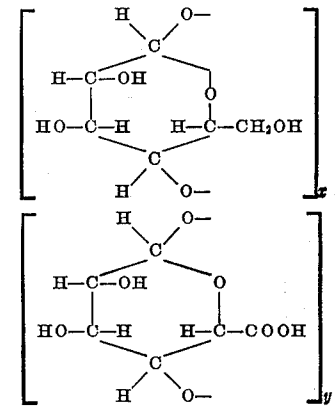
in the oxidation with NO_2—N_2O_4 gases and the secondary hydroxyls remain particularly unaffected. This is illustrated by the reaction formula:



wherein x and y may be any integer from 0 to 100, and $x+y=100$.

By restricting the attack of the oxidant, i. e., of NO_2—N_2O_4, to the specific hydroxyl groups in the cellulose molecule, degradation of the molecular chain is substantially avoided, while securing the chemical homogeneity of the reaction product. Furthermore, by preventing the occurrence of a topochemically variable reaction, physical homogeneity of the product is likewise obtained.

The selectivity of the NO_2—N_2O_4 oxidant for the primary hydroxyl of the anhydroglucose unit of cellulose permits of producing distinct and reproducible species of oxidized cellulose—the celluronic acids. Depending on the extent of oxidation, the resulting celluronic acids represent (1) polymers of anhydroglucuronic acid units in the case where the selective oxidation of the primary hydroxyl group is substantially complete, or (2) copolymers of anhydroglucose and anhydroglucuronic acid units, in the case where only a part of anhydroglucose units have been selectively oxidized by NO_2—N_2O_4 gases.

The completely oxidized celluronic acid has a theoretical carboxyl content of about 25.57% by weight based on the acid, while the celluronic acid with a carboxyl content of about 13.3% is a polymer of equimolar amounts of anhydroglucose and anhydroglucuronic acid units. In general, all

celluronic acids are characterized by a high affinity for dyes and readily absorb, e. g., methylene blue and rosaniline acetate.

Those celluronic acids which have a carboxyl content of more than about 11.5% by weight, though not directly soluble in water, form water-soluble salts with monovalent cations. On the other hand, when the carboxyl content of celluronic acids is more than about 7% but less than about 11.5% by weight, they are either insoluble or partly insoluble in dilute (1–2%) alkalies.

Now it has been discovered that the aforementioned celluronic acids, when partly or completely dissolved in dilute alkalies, or other monovalent bases, e. g., in aqueous pyridine, form salts which bring about an unexpected improvement in detergency, when added in small amounts to detergent mixtures. This improvement is remarkable, for these salts used alone in water possess no detergent effect, notwithstanding the amounts used. While the addition of these salts of celluronic acids to detergent compositions, for instance, to the alkaryl sulfonate mixtures, in amounts from about 0.5% by weight upwards, based on the total dry ingredients in the detergent mixture, results in an improvement of detergency, it has been found that the maximum effects are secured with amounts of about 3% and usually not greater than about 5% by weight. At this point, it may be noted that, although an addition of an amount greater than 3% by weight of a salt of celluronic acid to the detergent mixture exercises a definite improving effect upon detergency, the improvement thus obtained is usually equal or in some applications may be even lower than that obtained by an addition of 3% by weight, as will be shown by the explanatory experimental data hereinafter.

An additional unexpected discovery with respect to the monovalent cation salts of celluronic acids is the fact that a remarkable improvement in detergency is secured by the use of salts with the carboxyl content in the operative range of from about 7% to about 20% by weight, particularly in the critical range of from about 11.5% to about 18.5% by weight, that is, in the very range where celluronic acids become readily soluble in a 1% caustic solution.

It was indicated hereinabove that salts of celluronic acids may be prepared by reacting thereon with an aqueous solution of a monovalent base, e. g., dilute solution of sodium or potassium hydroxide. They may be also prepared by reacting celluronic acids with an aqueous solution of a salt of a weak acid, such as sodium carbonate.

To prepare a detergent composition improved in accordance with the present invention, the salt of celluronic acid in an amount of at least 0.5%, and preferably 3%, and usually not greater than about 5%, by weight of the total dry ingredients in the detergent mixture, is intimately dispersed in the detergent mixture supplied in a suitable form, e. g., as a slurry or a solution. Water is added, if necessary, to obtain the desired concentration of the mixture, and the resulting composition dried, e. g., by drum-drying, and recovered as a product having dispersed therein the required amount of the celluronic acid salt additive.

The term "dispersed" as used hereinabove means "intimately distributed," e. g., in the form of a colloidal dispersion, solution or emulsion within the detergent mixture.

The remarkable improvement in detergency

brought about by dispersing a small amount of a celluronic salt in a detergent composition is shown by the experimental data in the following Table I. The tests represented by these data are launderometer tests of soil removal from hard twisted cotton, the soil uniformly applied to the sample swatches of cotton being of an oily type (a paste of oil, tallow and carbon black). These tests are effected under conditions generally applied in common laundering processes, using procedures standardized to give reliable results which would be comparable to those of the actual practice. The temperature of the tests is about 140° F., though higher or lower temperatures do not affect the action of the celluronic acid salt additive. The hardness of water in all tests, unless otherwise specified, is the average hardness of water throughout the United States (300 parts per million=200 parts of calcium carbonate+100 parts of magnesium carbonate). In most tests, unless otherwise stated, 0.2% concentration of detergent mixture in water is used.

The several detergent compositions, which are used to compare the effect of an addition of the celluronic acid salt thereto with the detergency effects displayed without such an addition, include: a well-known anionic detergent composition comprising the salt of a half-ester of an alkenyl dicarboxylic acid designated as detergent X, an anionic mixture comprising sodium alkyl benzene sulfonate with 12 to 15 carbon atoms in the alkyl chain and produced by alkylating benzene with polypropene and designated as Detergent A, a non-ionic alkyl phenol polyglycol ether composition designated as Detergent Y, and an anionic sulfate of a fatty acid monoglyceride designated as Detergent Z. Sodium salt of celluronic acid with a carboxyl content of 11.5 to 18.5% in an amount of 5% by weight of the total dry ingredients of the detergent mixture is used.

The uniformly soiled swatches of cotton are subjected in each instance to a series of 4 consecutive washings of 20 minutes' duration, and the degree of whiteness obtained is measured in a photoelectric apparatus free of human equation. The detergency ratings in Table I are computed with reference to an arbitrarily chosen standard, namely, detergency (whiteness level) obtained with a 0.4% concentration of well-known soap D in hard water (300 parts per million), taken to be equal 100 and designated as Soap Index.

Table I

	Soap index
Detergent (X)	69
Detergent (X)+5% additive	78
Detergent (A)	53
Detergent (A)+5% additive	90
Detergent (Y)	76
Detergent (Y)+5% additive	115
Detergent (Z)	72
Detergent (Z)+5% additive	83

Another series of tests are carried out under similar conditions as for tests in Table I, but using a 0.2% concentration of detergent in soft water (50 parts per million of hardness, of which ⅔ is $CaCO_3$ and ⅓ is $MgCO_3$). In this series, several other detergents are used, namely, a well known alkyl sulfate detergent designated as Detergent B; a widely used type of soap D mentioned hereinbefore; another alkyl benzene sulfonate detergent of commerce designated as Detergent C; and an alkyl sulfonate composition designated as Detergent E.

The results of these tests are given in Table II and point to a definite improvement in detergency upon the addition of a salt of celluronic acid in accordance with this invention.

Table II

	Soap index
Detergent (A)	82
Detergent (A)+5% additive	96
Detergent (B)	77
Detergent (B)+5% additive	88
Detergent (D) (.4% conc.)	92
Detergent (D)+5% additive	105
Detergent (C)	75
Detergent (C)+5% additive	79
Detergent (E)	70
Detergent (E)+5% additive	76
Detergent (Y)	93
Detergent (Y)+5% additive	107

It is to be noted that the beneficial effects of the addition of a monovalent cation salt of a celluronic acid upon the detergency characteristics of a detergent composition are not limited to the compounds disclosed hereinabove, and that the improvement in detergency according to the present invention is obtained with other detergents, which embrace sulfonated oils, sulfonated and sulfated alcohols, sulfo-naphthenates, soaps of water-soluble amines, alkali soaps, aromatic sulfonates, sulfo-amides, sulfonated phenols and other anionic detergents, as well as non-ionic detergents, such as glyceryl esters of fatty acids, alkyl naphthol polyglycol ethers, polyethylene glycol ethers and the like. The only prerequisite for the effective application of salts of celluronic acids of the present invention is that the celluronic acid additive be capable of dispersion or solution in the detergent mixture.

Among the many detergent agents which may be improved by the application of the present invention, the alkaryl sulfonate-type detergents are found to constitute particularly suitable materials capable of a striking improvement in detergency upon the addition of small amounts of monovalent cation salts of celluronic acids.

These alkaryl sulfonates applicable for the preparation of the detergent compositions of the present invention contain an alkyl chain of not less than 8 and not more than 20 carbon atoms, directly linked to the aryl nucleus. Among these sulfonates, alkyl mononuclear aryl sulfonates, such as alkyl benzene sulfonates and alkyl toluene sulfonates, containing from not less than 8 to not more than 20 carbon atoms in the alkyl chain represent suitable ingredients for the preparation of the detergent compositions of the invention, a particularly desirable material being alkyl benzene sulfonates containing from 12 to 15 carbon atoms in the alkyl chain. These latter preferred sulfonates are obtained by alkylating benzene with polypropene, sulfonating the alkylate and neutralizing to form a water-soluble salt. Other materials than polypropene, e. g., polybutene or chlorinated kerosene, may be employed to alkylate the benzene ring prior to sulfonation and neutralization.

Suitable inorganic salts, e. g., sodium sulfate or sodium chloride, may be used to improve the sulfonate mixture, to enhance solubility and to insure a non-hygroscopic, non-caking detergent product. Generally, the proportion of sodium sulfate in the detergent mixture, depending on the particular intended application of the detergent, varies from 0 to 90% based on the total

weight of the dry sulfonate and sulfate ingredients, but preferably is greater than 50% and less than 80% by weight. The proportion of alkyl benzene sulfonate in the dry detergent mixture may be from 10% to 100% by weight of the total dry sulfonate-sulfate mixture (on additive-free basis, i. e., in the absence of the celluronic acid salt additive), and preferably less than 50% and at least 20% by weight. If so desired, other suitable inorganic alkali metal or ammonium salts, such as borates, phosphates, silicate, carbonates, and the like, may be incorporated as detergent extenders or builders. The alkali metal polyphosphates, such as tetrasodium pyrophosphate and sodium tetraphosphate, are particularly effective builders.

In the preparation of improved preferred detergent alkaryl sulfonate compositions of the present invention, an aqueous slurry, e. g., of sodium alkyl benzene sulfonate and sodium sulfate ingredients in a desired proportion is first prepared. Then at least 0.5%, and preferably 3%, and usually not more than about 5%, by weight based on the total dry ingredients of the detergent mixture of a sodium salt of celluronic acid is dispersed in this slurry in the required amount, and water is subsequently added, if necessary, to bring the concentration of the mixture to about 70% of water, whereupon the dry detergent is recovered by drum-drying. Of course, spray-drying and any other suitable technique of blending and recovering the improved detergent composition may be likewise employed within the scope of the invention. The dried product represents an intimate mixture of sodium alkyl benzene sulfonate and sodium sulfate, having dispersed therein a small amount of a sodium salt of celluronic acid.

The various advantages of the improved compositions of the present invention, and particularly of the preferred alkaryl sulfonate-type compositions are brought to light by the examination of experimental data presented hereinafter in the form of tables and graphs. The tests illustrated by these data are effected under conditions similar to those used in tests of Tables I and II. However, the amount of the sodium salt of celluronic acids added to improve detergency is equal to 3% by weight, unless otherwise indicated. The preferred alkyl benzene sulfonate detergent of the invention, containing from 12 to 15 carbon atoms in the alkyl chain and produced by alkylating the benzene ring with polypropene, comprises 40 parts of sodium alkyl benzene sulfonate to 60 parts of sodium sulfate on additive-free basis and similarly in Tables I and II is designated as Detergent A. Other designations of the various compositions tested are also the same as in Tables I and II.

In tabulating and plotting the experimental data, the detergency ratings for various detergents are computed either in terms of the percentage of soil removal or with reference to one of the two arbitrarily chosen standards: (1) detergency obtained with a 0.2% concentration of Detergent B in hard water (300 parts per million), assumed to be equal 100 and designated as Detergent Index; and (2) detergency obtained with a 0.4% concentration of soap D in hard water (300 parts per million), which has been used as a standard in Tables I and II hereinbefore.

Table III shows the differences in the improvement in detergency of the alkyl benzene sulfonate Detergent A of the present invention, occasioned by the addition of 3% by weight of sodium salt of

celluronic acids of varying carboxyl content. The existence of an optimum range of carboxyl content is readily perceived.

Table III

[97% Detergent A+3% additive]

Carboxyl Content in Per cent by Weight	Soap Index	Detergent Index
7.0	91	121
11.5	98	130
16.2	100	132
19.5	82	125
20.6	76	116

The data on soil removal assembled in Table IV again clearly show the existence of an optimum range of carboxyl content between about 11.5% to 18.5%.

Table IV

	Carboxyl Content in Per cent by Weight	Per cent Soil Removal
97% Detergent A+3% Additive	9.7	62
97% Detergent A+3% Additive	15.1	65
97% Detergent A+3% Additive	20.6	64
97% Detergent A+3% Additive	7.0	[1] 62*
97% Detergent A+3% Additive	11.5	[1] 65*
97% Detergent A+3% Additive	16.2	[1] 66*
97% Detergent A+3% Additive	19.5	[1] 62*
Detergent A alone		39
Detergent B alone		43
Soap D (.4% conc.) alone		61

[1] In tests marked with an asterisk, a purchased celluronic acid additive is used, while the remainder of tests employ a similar additive prepared in the laboratory.

In Table V are tabulated the values of soil removal in per cent obtained in still another series of tests. A 0.2% concentration of Detergent A is again used, and increasing increments of the sodium salt of celluronic acid are added thereto. The carboxyl content of the additive is from about 11.5 to about 18.5% by weight.

Table V

Sample	Total Concentration in Per cent (Detergent + Additive)	Per cent Soil Removal
100% Detergent A alone	0.200	51
100% Detergent A+0.5% additive	0.201	57
100% Detergent A+1.0% additive	0.202	61
100% Detergent A+2.0% additive	.204	63
100% Detergent A+3.0% additive	.206	66
100% Detergent A+4.0% additive	.208	66
100% Detergent A+8.0% additive	.216	65
100% Detergent A+10.0% additive	.220	65
100% Detergent A+15.0% additive	.230	63
Detergent B alone	0.2	42

As the additive used alone is found to have no detergent action in launderometer tests, the detergency improvement brought about by its presence in alkyl benzene sulfonate detergent mixture A is clearly evidenced by the above data in Table V.

Table VI contains the results of launderometer tests for varying total concentration of the improved detergent mixture and shows the increase in detergency resulting from the introduction of celluronic acid additive upon increasing the total concentration of the detergent mixture.

Table VI

Sample	Per cent Concentration	Soap Index
100% Detergent A alone	.15	24
97% Detergent A+3% additive	.15	89
100% Detergent A alone	.20	69
97% Detergent A+3% additive	.20	102
100% Detergent A alone	.30	71
97% Detergent A+3% additive	.30	107
100% Detergent A alone	.40	64
97% Detergent A+3% additive	.40	110

The next Table VII illustrates the effect of salts of celluronic acids on the detergency of various commercial products in hard water. All of the compositions tested show an improvement in detergency in the presence of the new additive of the invention. However, a truly remarkable improvement is observed only for alkyl benzene sulfonate Detergents A and C.

Table VII

Composition	Per cent Concentration	Soap Index
Detergent A	.2	44
Detergent A+3% additive	.2	63
Detergent B	.2	42
Detergent B+3% additive	.2	54
Detergent C	.2	37
Detergent C+3% additive	.2	61
Soap D (.4% concentration)	.4	62
Soap D+3% additive	.4	68

Table VIII contains additional data from similar tests with various commercial detergents, the detergency being evaluated in this instance in terms of the Soap Index mentioned hereinbefore. Here again the improvement occasioned by the presence of the celluronic acid additive is clearly apparent.

Table VIII

Composition	Soap Index
Detergent A alone	71
Detergent A+3% additive	103
Detergent B alone	69
Detergent B+3% additive	89
Detergent C alone	62
Detergent C+3% additive	100
Soap D alone (.4% concentration)	100
Soap D+3% additive	110

Table IX is introduced to show that the benefits obtained by the use of the salts of celluronic acids in alkyl benzene sulfonate detergent compositions are not limited to the particular 40/60 ratio of sulfonate to sulfate.

Table IX

Sample	Per Cent Soil Removal
60 % (97% sulfonate+3% additive) +40% Na_2SO_4	59
50% (97% sulfonate+3% additive) +50% Na_2SO_4	57
40% sulfonate (no additive) +60% Na_2SO_4	36
40% (97% sulfonate+3% additive) +60% Na_2SO_4	57
30% sulfonate (no additive) +70% Na_2SO_4	38
30% (97% sulfonate+3% additive) +70% Na_2SO_4	51

Table X shows the improving effect of the salts of celluronic acids on sulfonate/sulfate detergent mixtures containing a minor amount of an inorganic builder, such as tetrasodium pyrophosphate.

Table X

	Detergent index
100% detergent (no additive)	91
100% detergent+3% additive	172
90% detergent (no additive) +10% $Na_4P_2O_7$	104
90% detergent+3% additive+10% $Na_4P_2O_7$	143

It is to be noted that since the alkyl benzene detergent mixture used for these tests has the sulfonate/sulfate ratio of 40/60, the additive will produce no significant effect beyond the 60/40 ratio of the detergent mixture to pyrophosphate, as the effective concentration of sulfonate is then cut down to 24%, which in turn corresponds to a 0.048 concentration of the detergent, too low to produce any effect but that of the additional inorganic builder.

An additional series of tests is carried out to determine in terms of the Soap Index used hereinbefore the improvement in detergency brought about by the application of the improved compositions of the present invention to the removal of vacuum-cleaner dust-type soil from hard twisted cotton. This type of soil is obtained in the collector bags of conventional vacuum cleaners from cleaning rugs, overstuffed furniture and drapes. Same test conditions are applied as above, the hardness of water being 50 parts per million. The results are given in Table XI.

Table XI

	Soap index
Detergent Y	90
Detergent Y+5% additive	94
Detergent X	90
Detergent X+5% additive	106
Detergent A	74
Detergent A+5% additive	88

It is also observed that the addition of the sodium salt of celluronic acid enhances the removal of soil from wool fabric. A series of tests are carried out on wool soiled with an oily-type soil at 85° F. The hardness of water is 300 parts per million. The results indicate that there is an increase in soil removal averaging 5%. These results are tabulated in Table XII.

Table XII

	Concentration	Per cent soil removal
100% Detergent A	.15	8
97% Detergent A+3% additive	.15	10
100% Detergent A	.20	16
97% Detergent A+3% additive	.20	22
100% Detergent A	.30	49
97% Detergent A+3% additive	.30	56
100% Detergent A	.40	47
97% Detergent A+3% additive	.40	50

The invention is further illustrated by several figures which translates into graphs some of the tabulated data.

Fig. 1 graphically represents the data of Table III, while Fig. 2 corresponds to the data in Table V.

The consideration of the data presented in the description hereinabove reveals the following facts:

(1) Detergency characteristics of anionic and non-ionic detergents, in either soft or hard water, are markedly improved by the addition of a small quantity of a salt of a celluronic acid with a monovalent base;

(2) The most effective detergency improvers are those salts of a celluronic acid with a monovalent cation base, which have a carboxyl content from about 11.5 to about 18.5% by weight of the acid, though salts having a lower or a higher carboxyl content are also found to improve detergency;

(3) The alkaryl sulfonate type detergents and, in particular, those containing not less than 8 and not more than 20 carbon atoms, and preferably from 12 to 15 carbon atoms, in the alkyl chain, and obtained by alkylating benzene with polypropene, sulfonating the alkylate and neutralizing, are found to be exceptionally improved by the addition of small amounts of the aforementioned salts of celluronic acids;

(4) The addition of about 3% and usually not more than about 5% by weight of a monovalent cation salt of a celluronic acid, based on the weight of the dry detergent composition, secures the optimum improvement in detergency;

(5) Ordinarily, however, little or no additional detergency improvement can be achieved by the application of celluronic acid salts in amounts greater than about 3% by weight;

(6) The improvement due to the introduction of salts of celluronic acids of the present invention, is not affected by the presence of varying amounts of inorganic builders, such as sodium sulfate or tetrasodium pyrophosphate, provided the concentration of the detergent is not too low to produce any effect independently of the builder.

At this point, it must be pointed out that the invention is not restricted to the use of alkali metal salts of celluronic acids in detergent compositions. Other wholly or partly soluble salts of celluronic acids, produced, for instance, by dissolving them in dilute ammonia, warm aqueous pyridine, aqueous solutions of quaternary ammonium hydroxides, sodium carbonate or sodium acetate possess a like property of improving detergency.

The valuable improved detergent compositions of this invention are capable of numerous applications, namely, in laundering of textile fabrics and similar materials, in washing automobiles, various painted and metal surfaces, glass ware, ceramic ware, in dishwashing, window-washing and various other domestic and industrial uses.

It is to be understood that the aforegiven description and the experimental data are intended to be illustrative only, and that any variation or modification of the invention which conform with the spirit and the scope thereof is intended to be included within the terms of the appended claims.

I claim:

1. A detergent composition comprising an alkaryl sulfonate detergent containing from 8 to 20 carbon atoms in the alkyl chain and a minor amount of a water-soluble, alkali metal salt of a celluronic acid, sufficient to enhance the detergency characteristics of said sulfonate detergent and being from at least 0.5% to less than 50% by weight of the solid constituents thereof, the carboxyl content of said celluronic acid salt being from about 7 to about 20% by weight based on the acid.

2. A detergent composition comprising an alkyl monoaryl sulfonate detergent containing from 8 to 20 carbon atoms in the alkyl chain and a minor amount of a water-soluble, alkali metal salt of a celluronic acid, sufficient to enhance the detergency characteristics of said sulfonate detergent and being from at least 0.5% to less than 50% by weight of the solid constituents

thereof, the carboxyl content of said celluronic acid salt being from about 7 to about 20% by weight based on the acid.

3. A detergent composition, as defined in claim 2, wherein said alkyl monoaryl sulfonate contains from 12 to 15 carbon atoms in the alkyl chain, and said celluronic acid salt has a carboxyl content from about 11.5 to about 18.5% by weight based on the acid.

4. A detergent composition comprising a monoalkyl benzene sulfonate containing from 8 to 20 carbon atoms in the alkyl chain and a minor amount of an alkali metal salt of a celluronic acid sufficient to enhance the detergency characteristics of said sulfonate and being from at least 0.5% to less than 50% by weight of the solid constituents thereof, the carboxyl content of said celluronic acid salt being from about 7 to about 20% by weight based on the acid.

5. A detergent composition comprising a monoalkyl benzene sulfonate containing from 12 to 15 carbon atoms in the alkyl chain and a minor amount of an alkali metal salt of a celluronic acid, sufficient to enhance the detergency characteristics of said sulfonate and present in an amount from at least 0.5 to about 5% by weight based on the solid constituents of said sulfonate, the carboxyl content of said celluronic acid salt being from about 11.5 to about 18.5% by weight based on the acid.

6. A detergent composition comprising a monoalkyl benzene sulfonate containing from 12 to 15 carbon atoms in the alkyl chain and a minor

amount of a sodium salt of a celluronic acid, sufficient to enhance the detergency characteristics of said sulfonate and being from at least 0.5% to less than 50% by weight of the solid constituents thereof, the carboxyl content of said celluronic acid salt being from about 11.5 to about 18.5% by weight based on the acid.

7. A detergent composition comprising a polypropyl benzene sulfonate containing from 12 to 15 carbon atoms in the polypropyl chain and a minor amount of a sodium salt of a celluronic acid, sufficient to enhance the detergency characteristics of said sulfonate and being from at least 0.5% to less than 50% by weight of the solid constituents thereof, the carboxyl content of said sodium salt of celluronic acid being from about 7 to about 20% by weight based on the acid.

JOHN E. HANSON.

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