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DETERGENT COMPOSITIONS CONTAINING OXIDIZED POLYSACCHARIDE BUILDERS

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No Drawing. Continuation of abandoned application Ser. No. 802,255, Feb. 25, 1969. This application Nov. 17, 1971, Ser. No. 199,812

Int. Cl. C11d 3/02

U.S. Cl. 252—89 6 Claims

ABSTRACT OF THE DISCLOSURE

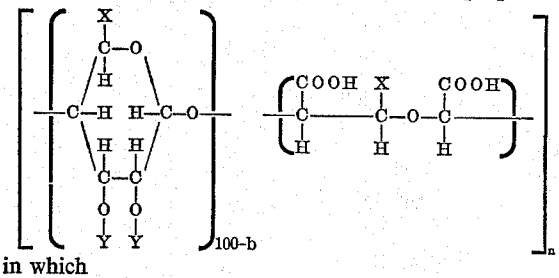
Detergent and laundering compositions comprising an organic water-soluble synthetic detergent and a water-soluble oxidized polysaccharide builder in a proportion by weight of detergent to builder of 10:1 to about 1:20; the builder having a degree of carboxylation of 1.0 to 3.0, an equivalent weight of 68 to 200, a degree of polymerization, *n*, of 20 to 30,000 and a molecular weight of 4,000 to 5,000,000.

This is a continuation of application Ser. No. 802,255 filed Feb. 25, 1969, and now abandoned.

This invention relates to detergent and laundering compositions which contain a water-soluble synthetic detergent and a so-called builder material. Such compositions are referred to in the art as built detergent and laundering compositions. The role of a surface active detergent in cleaning and soil removal from substrates such as soiled fabrics is well known. It is also well known that materials exist which when used in conjunction with detergents in a detergency system serve to provide improved cleaning results. Such detergency aids are called builders. The role of builders is described in detail in U.S. Pat. 3,159,581, issued on Dec. 1, 1964, to Francis L. Diehl and assigned to The Procter & Gamble Company. This patent is incorporated herein by reference and the specific discussion found in column 1, lines 13–72 and column 2, lines 1–3 provides background on the role and function of builders.

It has now been found that oxidized polysaccharides of the character described below provide useful builder properties when used in conjunction with organic synthetic detergents selected from anionic, nonionic, zwitterionic, ampholytic synthetic detergents and mixtures of such detergents.

The oxidized polysaccharide builders useful in the present invention have the following formula and properties:



in which

X is selected from —COOH, —CH_2OH, and —CH_2O—CH_2COOH

Y is selected from —H, and —CH_2COOH;

b is at least 10% by weight of the builder;

n represents the degree of polymerization and is an integer in the range, the lower limit of which is 20 and the upper limit of which is determined by the solubility characteristics in an aqueous system;

the degree of carboxylation is 1 to 3; and

the equivalent weight is from 68 to 200 calculated on the acid form.

The builder compounds of the present invention are oxidized derivatives of natural polysaccharide polymers of which the preferred embodiments are starch, cellulose and alginates. Such natural polymers are well known and are readily available commercially in natural form or in the oxidized form directly useful in the present invention. No novelty is ascribed herein to the process for preparing the oxidized polysaccharides noted above, only to the discovery of their usefulness as effective builders for organic synthetic detergents.

Inasmuch as the present invention applies to the area of detergent compositions and contemplates the uses of aqueous detergency systems, the upper limit on the degree of polymerization (D.P.) or *n* in the formula above is necessarily determined by the solubility characteristics of a specific builder polymer. As a general rule, however, the value for *n* is from 20 to 30,000. A preferred minimum value for *n* is 30.

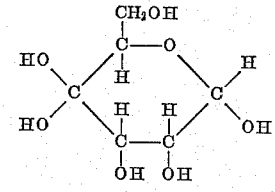
The molecular weight of these builder compounds range from 4,000 to 5,000,000 and preferably 25,000 to 2,000,000.

While the degree of carboxylation (D.C.) can be from 1.0 to 3.0, it is preferred that the degree of carboxylation exceed about 1.3. The maximum, in any event, is three.

In practice, the builder compounds are employed as water-soluble salts in which the cation is any water-soluble cation which does not interfere with the cleaning process. Preferred cations are alkali metals such as sodium, potassium and lithium; ammonium; substituted ammonium such as mono-, di-, and tri-methyl ethanol, and propanol ammonium cations; as well as amine and similar alkanol derivatives.

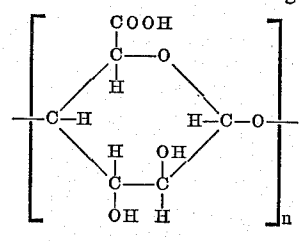
By "degree of carboxylation" is meant the number of carboxyl groups in the glucose or alginic acid monomer given above.

Glucose occurs in both alpha and beta forms and has the general formula:



The designations of alpha and beta forms relate, as is well known in the art, to different stereochemical configurations. While both starch and cellulose are comprised of such building blocks, it is also known that starch has both 1,4- and 1,6-links, while cellulose contains only 1,4-links. These different linkages do not appear to interfere substantially with the builder properties discovered and described herein. Moreover, the starch polymers can be straight chain or branch chain. Amylose is illustrative of a straight chain starch; amylopectin is an example of branched (1,6 links) starches. All are useful as builder embodiments according to the present invention.

Besides oxidized starches and celluloses, other polysaccharides are also useful such as alginic acid and pectic acid. These structurally similar acids are derived respectively from sea weed and fruits. Alginic acid is a preferred embodiment and has the following formula:



These are readily available commercially in several forms including carboxylated acid and salt forms. The value of *n* (degree of polymerization) is known to vary depending on well known preparative methods (extraction processes) and the source thereof.

In the oxidized polysaccharide general formula given above, the oxidized portion of the polysaccaride is indicated on the right-hand side of the formula. This portion (*b*) of the polymer constitute at least 10% by weight of the polymer builder compound and preferably should exceed 15%. The balance of the polymer (100%—*b*) consists of unoxidized polysaccaride units (starch, cellulose, alginic acid and the like). It is known in the art that the total polymer can be fully oxidized and such materials are also contemplated herein. The preferred value for *b* therefore is 15% to 100%.

In practice the oxidized polysaccharide builder compounds described and illustrated above are used in conjunction with organic synthetic detergents to provide laundering and detergent compositions.

The organic water-soluble synthetic detergents useful in the present invention include the anionic, nonionic, zwitterionic and ampholytic detergents which are illustrated and exemplified in great detail in U.S. Pat. 3,159,581, previously incorporated herein by reference. All of the compounds mentioned in that patent beginning at column 3, line 74 and extending to column 5, line 59 are incorporated herein. There are other examples which fall within the named classes of detergents and they are also useful herein. Olefin sulfonate detergents are an example of very useful detergents such as those described in U.S. Pat. 3,332,800 incorporated herein by reference.

In practicing the present invention, a detergent and laundering composition comprises an organic water-soluble synthetic detergent and a water-soluble oxidized, polysaccharide builder in a proportion by weight, respectively, of 10:1 to 1:20, and preferably 5:1 to 1:10. The composition can be prepared as liquids or solids formulations: Built liquid compositions having a liquid aqueous or alcoholic base are especially useful. Solid formulations such as tablets, granules, powders, flakes and the like find widespread application.

In a finished detergent formulation of this invention there will often be added in minor amounts materials which make the product more effective or more attractive. The following are mentioned by way of example. A soluble sodium carboxymethylcellulose may be added in minor amounts to inhibit soil redeposition. A tarnish inhibitor such as benzotriazole or ethylenethiourea may also be added in amounts up to about 2%. Fluorescers, perfume and color while not essential in the compositions of the invention, may be added in amounts up to about 1%. An alkaline material or alkali such as sodium hydroxide or potassium hydroxide can be added in minor amounts as supplementary pH adjusters. There might also be mentioned as suitable additives moisture, brightening agents, sodium sulfate, and sodium carbonate.

Corrosion inhibitors generally are also added. Soluble silicates are highly effective inhibitors and can be added to certain formulas of this invention at levels of from about 3% to about 8%. Alkali metal, preferably potassium or sodium, silicates having a weight ratio of

$$SiO_2M_2O$$

of from 1.0:1 to 2.8:1 will be used. M in this ratio refers to sodium and potassium. A sodium silicate having a ratio of SiO_2:Na_2O of about 1.6:1 to 2.45:1 is especially preferred for economy and effectiveness.

In the embodiment of this invention which provides for a built liquid detergent, a hydrotropic agent may at times be found desirable. Suitable hydrotropes are water-soluble alkali metal salts of toluenesulfonate, benzenesulfonate, and xylenesulfonate. The preferred hydrotropes are the potassium or sodium toluenesulfonates. The hydrotrope salt may be added, if desired, at levels of 0% to about 12%. While a hydrotrope will not ordinarily be found necessary, it can be added if so desired for any reason such as to produce a product which retains its homogeneity at a low temperature.

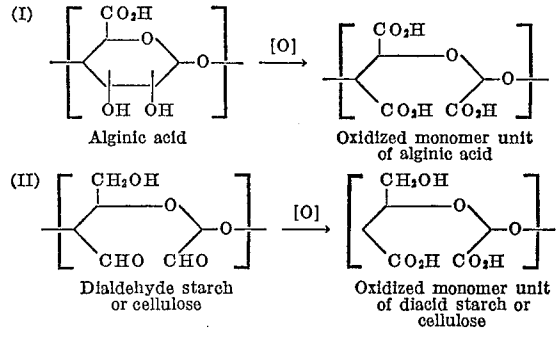
The detergent and laundering compositions of this invention provide best cleaning results when used in aqueous solutions having a pH of 9 to 12, preferably 9.5 to 11.5.

The compositions of this invention provide best cleaning results when used at a sufficient level to provide in solution a concentration of builder in the range of .02% to .5% by weight.

The oxidized polysaccharide builders which represent preferred embodiments are the oxidized starch derivatives, the oxidized cellulose derivatives and the oxidized alginate derivatives having the equivalent weights, the degrees of carboxylation, the molecular weights and the degrees of polymerization (*n*) described above.

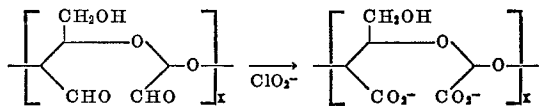
The oxidized polysaccharide builders as mentioned above can be prepared in any manner or used in the form commercially available.

A general equation to represent the oxidizing step is as follows



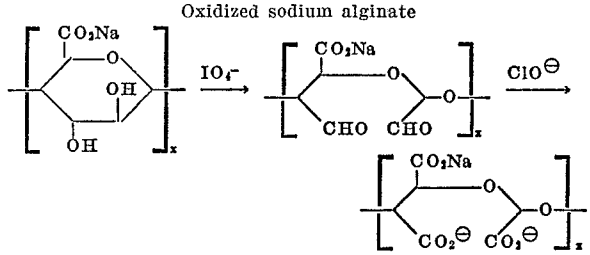
More specific preparative steps are given below as typical known reactions.

Oxidized dialdehyde starch (diacid starch)



The starting material for this preparation was Sumstar-S (Sumner Chemical Co.), a periodate oxidized starch which assayed 90% dialdehyde content. Sumstar-S (20.0 g., 0.11 equivalent) was added at temperature to 290 ml. of 1.0 molar sodium chlorite solution containing 8.5 ml. glacial acetic acid. After two hours stirring, the mixture was aerated to remove color and the pH adjusted to 8.3 with sodium hydroxide. The product was precipitated by pouring into ethanol. Following several such solution precipitation cycles for purification, the sample was dried in vacuo to give 18.8 g. of product which assayed to an equivalent weight (CO_2Na) of 177. This corresponds to an average of 1.3 carboxyl groups per monomer unit.

Oxidized sodium alginate



(a) Periodate treatment: Sodium alginate (Matheson) (25 g., 0.13 mole) and sodium periodate (41 g., 0.19 mole) were dissolved in 875 ml. cold water and stirred 48 hours at 0.5° C. The mixture was diluted with an equal volume of ethanol, the gummy precipitate collected and washed in ether. After several similar solution precipi-

tation cycles, the product was used for the chlorite oxidation steps.

(b) Chlorite oxidation: Essentially the same procedure as used for the chlorite oxidation of dialdehyde starch. This product assayed about 1.5 carboxyl groups per monomer unit.

The builder properties of the oxidized polysaccharide builders of the present invention are demonstrated by the following cloth swatch test. The detergency effectiveness of these compounds is demonstrated by washing naturally soiled cloth (desized print cloth) for ten minutes in an aqueous solution of a detergent composition containing sodium dodecylbenzenesulfonated detergent (concentration—0.3%) and a builder employed at a concentration of .03% and .06%. The wash solution has a pH of 10, 7 grains per gallon hardness at 140° F. No fluorescers, bleaches or antiredeposition agents were used. After washing, rinsing and drying the percent of lipid soil removed from the swatch during the washing process is calculated. The percentage of soil removed with the composition containing an oxidized polysaccharide builder was then compared with the percentage of lipid soil removed by washing with standard builders such as sodiumtripolyphosphate (STP) and potassium pyrophosphate. In that way the relative effectiveness of the builder compounds of the present invention are determined and demonstrated. A Tergotometer was used for the washing operation (Tergotometer testing is described in "Detergency Evaluation and Testing" by J. C. Harris, Interscience Publishers, Inc. (1954, p. 60)).

The results of this demonstration are given below in Table I. The usefulness of the builders which are representative of those embodied in the present invention is clearly demonstrated.

The oxidized polysaccharide builders used in this demonstration had the following properties.

Builder A:

Degree of carboxylation—1;
The value of *b* in the formula above—54%;
Degree of polymerization—*n*, 500–1000;
Molecular weight—88,000–176,000;
Equivalent weight—176.

Builder B:

Degree of carboxylation—1.44;
The value of *b* in the formula above—72%;
Degree of polymerization—*n*, 500–1000;
Molecular weight—88,000–176,000;
Equivalent weight—132.

TABLE I.—CLOTH SWATCH TEST

	.03%	.06%
STP	44.3	54.5
$K_4P_2O_7$	39.2	45.0
Builder:		
A		42.9
B	30.3	52.4
C	39.7	55.6

One of the desirable properties for a compound to be an effective builder for detergents is a property of sequester hardness ions in water. The oxidized polysaccharides are especially valuable in this respect. The test used to discover these properties is called a Swatch-Dip test which measures the relative sequestering ability of a builder to employing a fabric-swatch impregnated with soap and an aqueous solution containing a predetermined level of calcium hardness minerals. Briefly, the procedure calls for preparing the aqueous solution containing the hardness ions, at pH 10, and dipping into it or immersing in it a fabric-swatch which has been impregnated with a measured amount of soap. The swatch remains in the solution for a predetermined amount of time. A measurement is then made to determine the amount of free calcium which has been absorbed by the fabric-swatch. The identical procedure is then repeated but with a predetermined concentration of a sequestrant compound added to the aqueous solution containing the calcium ions. Measurements of absorbed calcium are again made and comparisons drawn. Differences between the amounts of calcium absorbed in tests with and without sequestrants, is attributed to the ability of the sequestrant to tie-up or sequester the calcium and thereby decrease the level of free calcium ion concentration available for absorption by the immersed fabric swatch. A percentage is obtained in this manner called "percent hardness retained by sequestrant."

Several tests were conducted in the manner and comparisons were made between sodium tripolyphosphate (STP), sodium citrate, and sodium pyrophosphate. They are three well-known builder compounds. Several oxidized polysaccharides, which are representative of the builder compounds of the present invention, were also tested. The results tabulated below clearly demonstrates the useful sequestering properties of oxidized starches, oxidized celluloses, and oxidized alginates. The specific oxidized polysacchardies evaluated are also characterized in the table.

	Equiv. wt. (as acid)	D.c.[4]	b=Oxidized portion, percent	n[5]	Mol. wt.	Percent hardness retained .03%	.04%	.06%
Oxidized:								
Starch	136	1.34	67	300–500	55,000–140,000	42.9	35.7	67.2
Cellulose	130	1.41	70	500–1,000	92,000–183,000	55.7	68.6	84.3
CMOS [1]	84	2.97	98.9	300–750	75,000–189,000	84.3	84.3	100
CMOS	99	2.44	72	300–750	72,000–181,000	72.9	85.8	97.2
CMOS	109	2.0	70	300–750	65,000–163,000	65.8	81.4	92.9
CMOC [2]	96	2.68	70	500–1,000	129,000–257,000	67.2	80.0	92.9
CMOC	115	1.79	70	500–1,000	103,000–205,000	75.8	82.9	94.4
CMOA [3]	138	1.31	15	750–1,500	136,000–272,000	50.0	60.0	64.4
CMOA	126	1.54	15	750–1,500	145,000–291,000	42.8	60.0	75.8
Sodium:								
Tripolyphosphate						81.4	84.4	91.4
Pyrophosphate						81.4	81.4	82.9
Citrate	64					51.4		58.6

[1] Carboxymethylated oxidized starch (sodium salt).
[2] Carboxymethylated oxidized cellulose (sodium salt).
[3] Carboxymethylated oxidized alginic acid (sodium salt).
[4] Degree of carboxylation.
[5] Degree of polymerization.

Builder C:

Degree of carboxylation—1.31;
The value of *b* in the formula above—15%;
Degree of polymerization—*n*, 750–1000;
Molecular weight—132,000–264,000;
Equivalent weight—138.5.

The builder effectiveness of the oxidized polysaccharides of the present invention are further demonstrated by a test involving detachable collars and cuffs. The wash-wear tests involved washing naturally soiled white dress shirts in the following manner. Shirts containing detachable collars and cuffs were worn by male subjects under ordinary conditions for two normal working days. Following

wear, the collars and cuffs were washed for ten minutes in a small agitator-type machine using solutions of the detergent compositions to be evaluated. The washing conditions were as follows: A detergent, sodium dodecylbenzene, used at a concentration of .03%. The builder being evaluated was used at a concentration of .10%. The washing solution had a pH of 10. The washing solution contained 7 grams per gallon hardness and had a temperature of 140° F.

After a washing and drying cycle the collars and cuffs were visually compared with similarly soiled collars and cuffs which were washed in a standard detergent composition under the same conditions. Visual comparisons were made which were converted and expressed on a scale of 0 to 10.

According to this demonstration sodium tripolyphosphate builder gave a score of 5.0. Builder C, described above, received a value grade of 3.9. The conclusion is that the oxidized sodium alginate builder performed almost on a par with sodium tripolyphosphate. A sodium pyrophosphate builder in this same test receives a value grade of 3.9 or 4.0. On this basis, the builder compounds of the present invention are comparable in performance to the pyrophosphate builders.

The following compositions illustrate this invention:

	Percent
Sodium dodecyl benzene sulfonate	17.5
Sodium oxidized starch having a degree of carboxylation of 2.0, and an equivalent weight of 100, a degree of polymerization of 1000 and an average molecular weight of 25,000	47.5
Sodium sulfate	14.0
Sodium silicate	8.0
Water	13.0

The oxidized starch can be replaced with an equal weight of sodium oxidized cellulose having a degree of carboxylation of 1.5, an equivalent weight of 116, an average molecular weight of 75,000 and a degree of polymerization of 1500. In addition, the sodium dodecyl benzene sulfonate can be replaced by sodium olefin sulfonates. In all cases an effective laundering composition is provided when used in a washing solution having a pH of about 10 and a washing temperature in the range of 100 to 160° F.

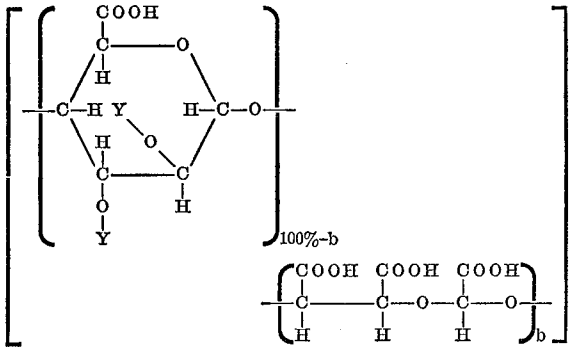
The foregoing description of the invention has been presented describing certain operable and preferred embodiments. It is not intended that the invention should be so limited since variations and modifications thereof will be obvious to those skilled in the art, all of which are within the spirit and scope of this invention.

What is claimed is:

1. A laundering and detergent composition consisting essentially of

(a) an organic, water-soluble synthetic detergent selected from the group consisting of anionic, nonionic, zwitterionic and ampholytic synthetic detergents and mixtures thereof;

(b) a builder compound which is a water-soluble salt of an alginic acid derivative, said alginic acid derivative having the general formula:



wherein

Y is selected from H and —CH_2COOH;

b represents the oxidized portion of the alginic acid derivative molecule and varies from 10% to 100%; and

n represents the degree of polymerization of the alginic acid derivative molecule and is an integer from 20 to 30,000;

said alginic acid derivative having a molecular weight of from 4,000 to 5,000,000; a degree of carboxylation of from 1.0 to 3.0; and an equivalent weight of from 68 to 200;

said synthetic detergent and said builder compound being present in a weight ratio of detergent to builder of 5:1 to 10:1; and

(c) from about 3% to about 8% by weight of the composition of an alkali metal silicate having a weight ratio of SiO_2 to alkali metal oxide of from 1.0:1 to 2.8:1.

2. A composition in accordance with claim 1

(a) wherein in the alginic acid derivative builder compound

(i) the degree of polymerization, *n*, varies from 750 to 1500;

(ii) the molecular weight varies from 25,000 to 2,000,000; and

(iii) the degree of carboxylation varies from 1.3 to 3.0; and

(b) wherein the alkali metal silicate is sodium silicate having a ratio of SiO_2 to Na_2O of about 1.6:1 to 2.15:1.

3. A composition in accordance with claim 2 which additionally contains up to 12% of a hydrotrope an alkali metal salt of an aromatic sulfonate selected from the group consisting of toluene sulfonate, benzenesulfonate and xylenesulfonate.

4. A composition in accordance with claim 2 wherein the alginic acid derivative builder is a carboxymethylated oxidized alginic acid having about 15% of the molecule oxidized; a molecular weight of from about 145,000 to 291,000; a degree of carboxylation of about 1.54 and an equivalent weight of about 126.

5. A composition in accordance with claim 2 wherein the alginic acid derivative builder is a carboxymethylated oxidized alginic acid having about 15% of the molecule oxidized; a molecular weight of from about 136,000 to 272,000; a degree of carboxylation of about 1.31 and an equivalent weight of about 138.

6. A composition of claim 2 in which the detergent is an anionic synthetic detergent.

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WILLIAM E. SCHULZ, Primary Examiner

U.S. Cl. X.R.

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