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DETERGENT COMPOSITIONS CONTAINING CARBOXYLATED POLYSACCHARIDE BUILDERS

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U.S. Cl. 252—89 1 Claim

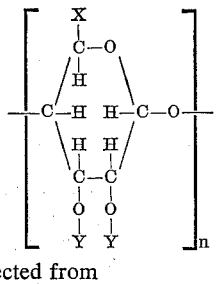
ABSTRACT OF THE DISCLOSURE

Deteregnt and laundering compositions comprising an organic water-soluble synthetic detergent and a water-soluble carboxylated alginic acid builder in a proportion by weight of 10:1 to about 1:20; the carboxylated builder having a degree of substitution of 1.3 to 2.0, an equivalent weight of 97 to 185, a degree of polymerization of 20 to 30,000 and a molecular weight of 4,000 to 5,000,000.

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 Proctor & 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 carboxylated 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 carboxylated polysaccharides builders useful in the present invention have the following formula and properties:



in which X is selected from

—COOH
—CH_2OH, and
—CH_2OCH_2COOH

Y is selected from

—H, and
CH_2COOH

n is a whole integer in a range, the lower limit of which is 20 and the upper limit of which is determined primarily by the solubility characteristics in an aqueous system; the degree of substitution is 1.3 to 3.0; and the equivalent weight is from 97 to 185, calculated as the acid form.

The builder compounds of the present invention are

derivatives of natural polymers of which the preferred embodiments are carboxylated starches, celluloses and alginates. Such polymer materials are well known and are readily available commercial materials having widely different chemical and physical properties.

Inasmuch as the present invention applies to the area of detergent compositions and contemplates the use 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.

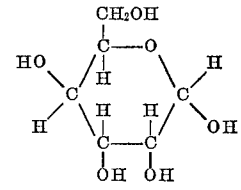
The molcecular weight of these builder compounds range from 4,000 to 5,000,000 and preferably 25,000 to 2,000,000.

While the degree of substitution (D.S.) can be from 1.3 to 3.0, it is preferred that the degree of substitution exceed about 1.5. The maximum, in any event, is three for the monomeric glucose structure given above.

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-methylol, ethanol, and propanol ammonium cations; as well as amine and similar alkanol derivatives.

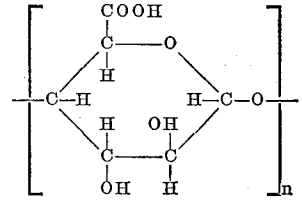
By "degree of substitution" is meant the number of carboxyl groups in the glucose or alginic acid monomer given above.

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



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. It is obvious from the structural formula above that the maximum degree of substitution of alginic acid is 2.

In practice the carboxylated 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. 3,332,880, incorporated herein by reference.

A useful property associated with effective builder compounds is a capability of sequestering hardness ions. This same property is provided by water softener compounds employed as detergency aids in conjunction with synthetic detergents. The test used to discover these properties is called a Swatch-Dip test which measures the relative sequestering ability of a builder by 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 "% hardness retained by sequestrant." Several demonstrations were conducted in this manner using sodium tripolyphosphate; sodium pyrophosphate; and sodium citrate. In addition, a carboxymethylcellulose polymer (Hercules) was evaluated having a degree of substitution of .67, an equivalent weight of 300, a degree of polymerization of 1200, a molecular weight of about 240,000, and a specific viscocity at .06% solution of sodium salt, 60° C. of .622. The carboxylated polysaccharide builder representative of the present invention used in this demonstation was a sodium carboxymethylcellulose having a degree of substitution of 1.5, an average degree of polymerization of 1500–2000, an average molecular weight of about 300,000 to 400,000, and an equivalent weight of 162.5.

This demonstration showed that the carboxylated polysaccharide builders of this invention had very useful sequestering properties. At a concentration of .06% it was substantially equal to the STP, pyro and citric acid. Moreover, it was shown to be far superior to the CMC sample tested which had a D.S. of only .67. The sequestering properties of all of the samples demonstrated were less at a concentration of .03%. Nevertheless, the builder of the present invention remained superior to the CMC having the .67 D.S. The results of this demonstration are given in Table I below:

TABLE I

Builder tested	Percent hardness retained by sequestrant .03%	.06%
1--- Carboxylated cellulose polysaccharide (D.S.=1.55)	27.1	48.6
2--- STP	38.6	47.2
3--- Sodium pyrophosphate	38.6	47.2
4--- Sodium citrate	41.4	45.7
5--- Hercules sodium carboxymethylcellulose (D.S.=.67)	24.3	25.7

The sequestering properties of numerous carboxylated derivatives of starch, cellulose, destrin, crystallized cellulose forms, corn starch, amylose, and alginic acid were demonstrated. The tests demonstrated conclusively the usefulness of these carboxylated polysaccharides as sequestering agents and builder compounds.

The effectiveness of the builder compounds of this invention is demonstrated by a detergency test referred to as a facial swatch test. This test involves a procedure of soiling a cloth swatch with natural soil by attaching a swatch (about 5 inches by 5 inches) to the plunger cup of an electric vibrator massager. Two swatches are soiled from an individual subject by massaging the right and left halves of the face respectively for one minute each. The resulting soiled swatches are randomized into different groups to statistically provide equal numbers of left and right samples. The swatches are then washed, rinsed and graded and the cycle is repeated nine times. The washing step consists of laundering the soiled swatches in an aqueous solution having a temperature of 140° F., a pH of 10, and containing 7 grains hardness.

A mechanical washer is used which is equipped with an agitator and otherwise simulates an ordinary home washing machine. The detergent compositions tested consisted of an active synthetic detergent at a concentration of .03% in the wash water and a builder ingredient at a concentration of 0.5%. The builders tested were compared with sodium tripolyphosphate, an excellent and widely used commercial builder. Following the washing of the soiled swatches, they were rinsed and dried and then whiteness measurements were made with a commercially available photoelectric reflectometer, i.e., a Hunter Color and Color Difference meter manufactured by Henry A. Gardner Laboratory, Inc. This instrument is designed to distinguish color differences and operates on the tristimulus colorimeter principle. According to this principle, a 45 degree diffuse reflectance of an incident light beam on a test specimen is measured through a combination of green, blue and amber filters. The electrical circuitry of the instrument is so designed that lightness and chromaticity values for the test specimen are read directly. The departure from white (TiO_2 being taken as a standard white) of the test specimen is calculated by introducing the lightness and chromaticity values so obtained into a complex formula supplied by the manufacturer. An evaluation of relative whiteness performance compared to a standard detergent composition is thus obtained for the test formulations. A more comprehensive description of this device and its mode of operation appears in Color in Business, Science and Industry by Deanne B. Judd, pages 260–262; published by John Wiley & Sons, New York (1952).

Two carboxylated polysaccharides representative of the cellulose and starch derivatives of this invention were compared to STP. The sodium carboxymethyl cellulose had an equivalent weight of 139 as the acid form, a molecular weight of about 300,000, a degree of substitution of 2.0, and an average degree of polymerization of 930. The sodium carboxymethylstarch derivative had an equivalent weight of 120, a molecular weight of 17,000 to 200,000, an average degree of substitution of 2.7, and an average degree of polymerization of about 53 to 620. The carboxymethylstarch derivative gave cleaning results

substantially equal to the STP. The carboxymethylcellulose derivative, while less effective than the starch derivative and the STP, still demonstrated highly useful and desirable builder properties.

While chemicals containing carboxylate groups have been known to be efficient builders such as sodium nitrilotriacetate (NTA) and ethylenediaminetetraacetates (EDTA), no natural polymers such as carboxylated starches, celluloses, and alginates have been used as detergency builders. One possible reason for this may be the fact that the cellulose derivatives which are conventional soil suspending agents have been shown to be ineffective builders when used at usual builder concentrations. Carboxymethylcellulose used as a soil suspending agent has a degree of substitution in the range of .5 to about .9, typically .6. It has not heretofore been realized that an effective class of builder compounds could be provided by increasing the degree of substitution to above 1.3 and especially about 1.5. Moreover the essential corollary aspects of equivalent weights, molecular weights and degree of polymerization as described above have not been fully appreciated.

In practicing the presnt invention, a detergent and laundering composition comprises an organic water-soluble synthetic detergent and a water-soluble carboxylated polysacharide builder in a proportion by weight respectively, of 10:1 to 1:20, and preferably 5:1 to 1:10. The compositions can be prepared as liquid or solid 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, enzymes, 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 is 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 toluene sulfonate, 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 carboxylated polysaccharide builders which represent preferred embodiments are the carboxylated starch derivatives, the carboxylated cellulose derivatives and the carboxylated alginate derivatives having the equivalent weights, the degrees of substitution, the molecular weights and the degrees of polymerization (n) described above.

The following compositions illustrate this invention:

17.5% sodium dodecyl benzene sulfonate
47.5% sodium carboxymethylcellulose (CMC) having a degree of substitution of 2.0, an equivalent wieght of 120, an average molecular weight of 400,000, and a degree of polymerization of 1500.
14.0% sodium sulfate
8.0% sodium silicate
13.0% water

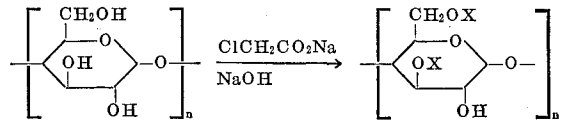
The CMC derivative can be replaced with an equal weight of sodium carboxymethylstarch having a degree of substitution of 2.7, an equivalent weight of 150, an average molecular weight of 1,000,000 and a degree of polymerization of 10,000. The result is a useful and highly effective built detergent composition.

In the preceding composition, one-half of the sodium carboxymethylcellulose can be replaced with sodium tripolyphosphate and an excellent built laundering composition is provided.

The present invention contemplates built detergent compositions in which a portion of the more traditional and widely used builders such as the polyphosphates, pyrophosphates, nitrilotriacetates, and phosphonates are replaced with the carboxylated polysaccharides (starches, celluloses, alginates, etc. having a high degree of substitution) described herein.

The carboxylated polysaccharides described herein are known compounds and readily available commercially. Moreover, ordinary chemical texts describe suitable techniques for synthesizing the desired compounds. A good description is given in Methods in Carbohydrate Chemistry, R. L. Whistler, Academic Press, New York, 1963, vol. III, pp. 322–327.

An equation for these carboxylating reactions is given:



X=CH_2CO_2Na or H

In the initial stage, 10.0 g. (0.06 mole) of the polysaccharide (e.g., starch) and 14.2 ml. of water are shredded in a blender for approximately 10 minutes. To this is added 8.2 g. (0.206 mole) of ground sodium hydroxide and blended for 10 min. Then 24.8 g. (0.212 mole) of sodium chloroacetate is added, the mixture is shredded for another 10 min., and is then allowed to stand, with occasional blending, until all of the sodium chloroacetate is reacted. This constitutes one treatment. Usually, each treatment is carried out for two or three days, and 5 or 6 treatments are required in order to obtain degrees of substitution (D.S.) of greater than 2. Lesser D.S.'s can be obtained in fewer treatments. From time to time during the preparation of the products enough water is added to the reaction mixture to maintain a pasty consistency.

After completion of the reaction, the mixture is dissolved in a minimal amount of water and the product is then precipitated by the addition of an excess of methanol. The product is collected by filtration or by decantation of the aqueous phase, redissolved in water, and then the precipitation-isolation procedures are repeated. Further purification, if desired, can be accomplished by trituration with hot methanol, and/or dialysis, and/or Sephadex® gel filtration.

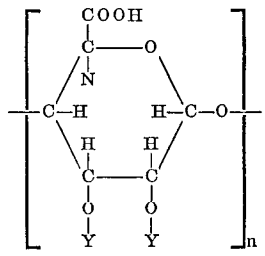
Analysis can be carried out by dissolving a weighed amount of the product in water, passing this solution over

a column of a strongly acidic ion exchange resin, and then titrating the resulting eluant with standardized sodium hydroxide solution.

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 detergent composition consisting essentially of an organic water-soluble detergent selected from the group consisting of anionic, nonionic, zwitterionic, ampholytic detergents and mixtures of such detergents, and a water-soluble carboxylated alginic acid derivative builder salt, the ratio by weight of said detergent to said builder salt being 10:1 to 1:20, said builder having the formula and properties as follows:



wherein Y is selected from —H and —CH_2COOH; n is a whole integer in a range, the lower limit of which is 20 and the upper limit of which is determined primarily by the solubility characteristics in an aqueous system; the degree of substitution is 1.3 to 2.0; and the equivalent weight is from 97 to 185, calculated as the acid form.

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