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[54] **BUILDER FOR PHOSPHATE-FREE DETERGENT COMPOSITIONS**

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[57] **ABSTRACT**

A detergent composition including an anionic or nonionic surfactant and a novel, hydrophilic but water-insoluble building agent comprising natural cellulose fibers having chemically bonded therein and thereon by in situ polymerization, an alkali salt of polyacrylic acid or polymethacrylic acid.

4 Claims, No Drawings

BUILDER FOR PHOSPHATE-FREE DETERGENT COMPOSITIONS

BACKGROUND OF THE INVENTION

This invention relates to detergent compositions and particularly to an improved component of such compositions commonly referred to as a builder.

Commercially available detergents are blends of a variety of components, each of which contributes to the overall cleaning efficiency of the detergent in aqueous solutions. Thus, all modern detergent compositions contain, in addition to one or more surface active components known as surfactants, certain additive components which enhance the cleaning power of the surfactive ingredients by performing one or more of several important functions, including: inactivating polyvalent metal ions such as calcium, iron and magnesium normally present in the water, preventing redeposition of soil on the article being washed, preventing corrosion of washing machinery, imparting a whitening or brightening effect to fabrics, and others.

A primary building agent of substantially all modern detergents is sodium tripolyphosphate, a compound which has been severely scored as an undesirable pollutant of the water resources of this and other countries by virtue of its nutritional contribution to the growth of deleterious plant and animal life in fresh water lakes and streams.

It is therefore of considerable interest to our overall ecology to find and utilize in detergent compositions a suitable substitute for the sodium tripolyphosphate builder normally incorporated therein. A number of phosphate-substitute builders have been proposed and utilized to limited extents but none has been completely satisfactory.

SUMMARY OF THE INVENTION

We have now found that an effective and completely satisfactory detergent building agent may be produced by polymerizing acrylonitrile or one of a number of other acrylic acid or methacrylic acid derivatives in the presence of cellulose fibers from wood pulp under conditions which promote the formation of a polymer of the chosen monomer within and on the surface of the cellulose fibers by a process of graft polymerization, treating the resulting product as required to produce alkali salts of polyacrylic acid or polymethacrylic acid on the fibers and drying and grinding the reaction product to a fine powder. The product of this process is a cellulose fiber having an acrylate or methacrylate polymer salt intimately bound therein and thereon and having excellent properties as a detergent builder, both in its function as a water softening agent and as an agent to prevent the re-precipitation of soil loosened and removed from a fabric by the surface active components of a detergent composition.

The detergent builder of this invention is also compatible with the other ingredients of customary detergent compositions and is completely stable both toward bleaching agents often utilized in connection with detergents and also in the presence of the hot, alkaline, aqueous medium used in many washing operations, including the washing of fabrics, glassware, dishes and the like.

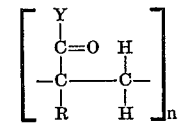
It is, therefore, an object of this invention to provide an improved building agent for use in synthetic organic detergent compositions.

It is a further object of this invention to provide an improved detergent builder which is effective in combination with anionic and/or non-ionic organic surface active compounds in detergent compositions.

Further objects will become apparent from the following description.

DETAILED DESCRIPTION OF THE INVENTION

In brief, the polymer modified fibers used in the practice of the invention are cellulosic fibers having deposited in situ therein a synthetic polymer of the general formula:



in which:

R is a hydrogen atom or a methyl group,

Y is OH or OM,

M is an alkali metal or ammonium ion, and

n is an integer greater than 500.

Various reactions producing the desired polymers will be immediately apparent to those skilled in the art. Examples of such methods are listed herein, but this list in not intended to be exhaustive:

1. Polymerize acrylonitrile in the fibers and hydrolyze with an alkaline solution to form alkali salts of polyacrylic acid.
2. Polymerize methyl acrylate in the fibers and hydrolyze with an alkaline solution to form alkali salts of polyacrylic acid.
3. Polymerize ethyl acrylate in the fibers and hydrolyze with an alkaline solution to form alkali salts of polyacrylic acid.
4. Polymerize acrylic acid or alkali salts of acrylic acid in the fibers.
5. Polymerize methacrylonitrile in the fibers and hydrolyze with acids to form polymethacrylic acid or hydrolyze with an alkaline solution to form alkali salts of polymethacrylic acid.
6. Polymerize methacrylic acid or alkali salts of methacrylic acid in the fibers.
7. Polymerize acrylamide in the fibers and hydrolyze with an alkaline solution to form alkali salts of polyacrylic acid.
8. Form copolymers of any of the above monomers or copolymerize with a small amount of non-hydrolyzable monomers.

For purposes of the present specification and claims, "alkali salts" are defined to include the alkali group metal salts and ammonium salts.

The detergent builder of the present invention comprises natural cellulose fibrous material having the selected monomer polymerized therein and thereon by an in situ polymerization technique in amounts ranging from less than 50 parts of polymer per 100 parts to cellulose to more than 500 parts of polymer per 100 parts of cellulose, all quantities mentioned above and throughout this description being given in weight units. The resulting polymer-grafted material is then subjected to further treatment, as necessary, to achieve conversion of the polymer to an alkali salt of polyacryl-

ic acid or polymethacrylic acid, as mentioned hereinbefore. If, for example, polyacrylonitrile is formed in the polymerization step, the polymer-grafted fibrous material is then treated with hot, aqueous alkali to effect a hydrolytic conversion of from about 40–85 percent of the nitrile groupings present on the polymer to carboxylate groups (ammonia being released during the hydrolysis) and the resulting product is dried and pulverized. The nitrogen content of the acrylonitrile groupings in the polymer which remains in the material after hydrolysis is presumed to have been converted by the hydrolysis from the nitrile form into corresponding amido groupings. The hydrolysis product, which consists of hydrolyzed polyacrylonitrile formed on and in the fibrous cellulose base material, thus contains substantial amounts of carboxylic acid groups (in the form of alkali salts of polyacrylic acid) as well as amido groups as a result of the alkaline hydrolysis. The product may be utilized as a detergent builder in aqueous suspension as the alkali salt, or dried and powered as mentioned above, or the hydrolysis reaction product mixture may be neutralized with a suitable mineral acid, such as hydrochloric acid, and then dried. In the latter case, of course, the dried product will also contain the alkali salt of the mineral acid used in the neutralization of the reaction liquor.

The following Example 1 describes in detail the method used for the preparation of the detergent builder of this invention by polymerization of acrylonitrile on wood pulp followed by hydrolysis of the resulting polymer-grafted material.

EXAMPLE 1

100 parts of bleached aspen kraft wood pulp were slurried in 2,700 parts of deionized water in a reactor equipped with a spiral ribbon agitator. After mixing 15 minutes to break up fiber clumps, 0.3 parts of ferrous ammonium sulfate hexahydrate were added and the slurry pH adjusted to 3.7 by the addition of sulfuric acid of 10 percent concentration. 180 parts of acrylonitrile, inhibited by the inclusion of 30 parts per million of hydroquinone mono methyl ether, were mixed with the pulp slurry and the reaction mass was heated to 78° C. to reflux the acrylonitrile and purge air from the reactor. After 5 minutes of reflux, heating was discontinued and 10 parts of 10 percent hydrogen peroxide were added to initiate the polymerization of acrylonitrile in and on the cellulose wood pulp fibers. The reaction was exothermic and proceded under reflux with no further requirement for added heating. After 45 minutes at reflux temperature, the unreacted acrylonitrile was distilled off in a typical stripping operation and the polymer-grafter fibers recovered by filtration and washing. The recovered fibers had 108 parts of polyacrylonitrile intimately chemically bonded to the cellulose, both on the surface thereof and within the structure of the fibers. Varying amounts of polymer may be structurally united with a given amount of wood pulp fibers by varying the monomer-to-fiber ratio in the reaction mixture. For example, if 400 parts of acrylonitrile are substituted in the above recitation of reactants, the resultant polymer-grafted fibers will retain from 200 to 250 parts of polymer for 100 parts of fiber, and further changes in the ratio of the reactants will be reflected in kind (although not in exact proportion) in the polymer-fiber ratio in the product.

EXAMPLE 2

In order to hydrolyze the polyacrylonitrile on the fibers, 100 parts of the polymer-grafted pulp product of Example 1 were slurried in 1,850 parts of water containing 50 parts of sodium hydroxide and the mixture held at 90° C. for 90 minutes, provision being made for the escape of ammonia gas formed by the hydrolysis reaction.

The resulting fibrous, hydrophilic, but water-insoluble hydrolysis product, may be utilized directly in the form of a 5 percent aqueous suspension of paste-like consistency as the building component for detergent compositions, or may be treated by any of several procedures for the recovery and utilization of the solids content as illustrated by the following examples. For convenience, the hydrolysis product of wood fibers containing polyacrylonitrile is referred to hereinafter as HPAN grafted fibers.

EXAMPLE 3

100 parts of the polymer-grafted cellulose pulp product of Example 1 were slurred in 1,850 parts of water containing 50 parts of sodium hydroxide and the mixture held at 90° C. for 90 minutes to accomplish the hydrolysis. The resulting 5 percent paste-like aqueous suspension was dried in an oven and placed in a ball mill for 6 hours to grind the polymer grafted-fibers to a fine powder which passed through a standard 325 mesh screen (indicating a particle size of less than about 44 microns in diameter). The resulting water-insoluble, powdered fibrous product was found to be an effective detergent builder as will be fully described hereinafter.

EXAMPLE 4

100 parts (dry basis) of the polymer-grafted cellulose pulp product of Example 1, taken after the washing step and containing between 50 and 60 percent solids and 40–50 percent water, were placed in a ribbon mixer at 90° C. and 50 parts (dry basis) of sodium hydroxide were slowly added as a 30 percent aqueous solution. After 90 minutes at 90° C., the crumbly hydrolyzed product (containing nearly 60 percent solids) was oven dried and ball milled to a fine, water-insoluble powder which was then utilized as a detergent builder as hereinafter described. It has been found that the hydrolysis product, as obtained by carrying out the hydrolysis in the high solids concentration described in this Example, may be more readily dried and ground to a particle size suitable for use as a detergent builder than when the hydrolysis step is carried out at a relatively low solids concentration (5 percent solids) as described in the previous Example. The product of the high solids hydrolysis is obtained as a crumbly, highly porous moist mass of high surface area somewhat ressembling crumbs of foamed plastic. In this physical state, the product is easily dried in an oven at temperatures from about 50° to about 105° C. to yield a friable solid which may be readily ground or ball milled to a fine powder which is readily re-wet by water.

By way of comparison, the product obtained in the hydrolysis carried out at 5 percent solids concentration is far more difficult to dry uniformly and the dried product is quite hard, dense and difficult to grind to a powder form. Furthermore, the powder which is obtained is somewhat less readily re-wet by water than

that obtained from the high solids hydrolysis procedure, although the product in either case is of substantially equal effectiveness as a detergent builder.

In general, in the preferred procedure for carrying out the hydrolysis step, the total solids content of the reaction mass, including both the polymer-grafted fibers and the caustic reactant, should be at least 25 percent and preferably about 40–50 percent. If the total solids content at this point is higher than about 60 percent, it has been found difficult to obtain uniform blending of the reactants and the hydrolysis reaction does not proceed as smoothly as desired. As hydrolysis proceeds at 80–100° C., some water is allowed to evaporate and the final, hydrolyzed reaction mass will preferably have a solids content approaching about 60 percent. The hydrolyzed polymer-grafted fibers produced in this manner may be dried and pulverized very easily due to their friable nature to form a powder which is readily re-wet by water and is quite suitable for use as a detergent builder.

EXAMPLE 5

100 parts of the polymer-grafted cellulose pulp product of Example 1 were hydrolyzed for 90 minutes at 90° C. with 50 parts of caustic soda in 1,850 parts of water. Hydrochloric acid was added to bring the reaction mixture to neutrality, 50 parts of sodium carbonate were added and the resulting mixture dried and ball milled to a fine powder, which was found to be an effective detergent builder as described hereinafter.

To determine the effectiveness of the hydrolyzed polyacrylonitrile grafted cellulose fiber material (HPAN grafted fibers) as a detergent builder, tests were conducted wherein standard soiled fabric samples were subjected to a standardized washing cycle in a Tergotometer washing device, utilizing water of predetermined hardness and with the addition of specified proportions of a standard surface active agent (anionic or non-ionic) commonly utilized as the surface active base ingredient of a variety of commercial detergent compositions. The tests compared the effectiveness in soil removal of the washing compositions containing the product of this invention with those containing various standard detergent builders commonly utilized in commercial detergent compositions.

The following is a detailed description of the test procedure for determining soil removal effectiveness of a given detergent composition as carried out in a series of experiments, the results of which are presented in tabular form hereinafter.

The following standard fabric samples were utilized in washing tests, as indicated in the tables presented hereinafter.

1. Cotton Soiled Test Cloth No. 26 with unsoiled borders for U. S. Naval Spec. 51 S 47 (IMT) Bureau of Ships, obtained from Testfabrics, Inc., New York, N.Y.
2. EMPA Standard Soiled Cotton Fabric, obtained from Test-fabrics, Inc., New York, N.Y.
3. Standard Soiled Cotton Test Cloth, obtained from U. S. Testing Co., Hoboken, N.J.
4. Standard Unsoiled Cotton Test Cloth, obtained from U. S. Testing Co., Hoboken, N.J.

The washings were carried out in a Model 7243 Tergotometer obtained from U. S. Testing Co., Hoboken, N.J. The spinning cycle after washing and rinsing was carried out in a Model 0510/0512 Hoover Portable Washer. Surface brightness of the fabric was measured by a standard Paper Brightness Meter, Model S–1, obtained from Martin Sweets Co., Louisville, Ky. A stock water hardness solution containing 40,000 ppm of calcium and magnesium salts was prepared by dissolving 35.0 gm. of calcium chloride dihydrate and 32.8 gm. of magnesium chloride hexahydrate in distilled water and diluting to 1,000 ml. of solution.

Washing in the Tergotometer is carried out in stainless steel beakers of 2,000 ml. capacity partially immersed in a water bath maintained at 140° F. Agitators within the beakers are operated at 100 cycles per minute. A wash water of 400 ppm hardness is prepared in each beaker by adding 10 ml. of the stock water hardness solution to 1,000 ml. of water warmed to 140° F. The detergent composition to be tested is added to the wash water and after two minutes of mixing to insure uniformity, two 4×9 inch swatches of the selected test fabrics as noted above are placed in each beaker and are washed for 15 minutes. The sample swatches are then transferred to the spin dry section of a Hoover portable washer and are subjected to a two minute spin cycle. The damp sample swatches are then rinsed in 1,000 ml. of cold tap water in the Tergotometer under agitation for five minutes and spin dried in the Hoover washer for 2 minutes. The rinsing and spin dry cycles are repeated and the washed swatches are dried at room temperature and ironed smooth with a warm flat iron.

The surface brightness of the various samples is measured by the procedure used in TAPPI Standard Method T–452–M58 for measuring paper brightness, using the Paper Brightness Meter previously mentioned or an equivalent instrument.

In determining the effectiveness of a tested detergent composition, the present detergency is calculated as follows:

Percent Detergency $=(100\,(C-B))/(A-B)$

Loss in Brightness $= A-D$

Where A = Brightness of unwashed, unsoiled cloth
B = Brightness of unwashed, soiled cloth
C = Brightness of washed, soiled cloth
D = Brightness of washed, unsoiled cloth

EXAMPLE 6

In order to demonstrate the effectiveness of the detergent builder of the present invention in comparison with that of other materials commonly utilized as builders in commercially available detergent compositions, washing tests as hereinbefore described were carried out using wash waters of 400 ppm hardness and containing 0.025 percent of a standard, high quality, nonionic surface active agent (Tergitol 15–S–9, a polyethylene glycol ether of linear alcohols having a chain length of between 11 and 15 carbon atoms. Tergitol is available from the Union Carbide Corporation) and 0.15 percent of the specific building agent being tested. Detergency and brightness test results are tabulated in the following Table I. Control tests were also run wherein the wash water contained the surfactant but no builder, and wherein the wash water contained neither surfactant nor builder.

TABLE I

COMPARISON OF DETERGENT BUILDERS

Building Agent	% Detergency Test fabric Cloth	% Detergency U.S. Testing Cloth	Brightness of Unsoiled Cloth After Washing
Control (No Surfactant, No Builder)	16	4	82
Control (Surfactant Alone, No Builder)	20	20	68.2
Sodium Tripolyphosphate	38	21	71.3
Sodium Nitrilotriacetate	38	21	71.3
Carboxymethyl Cellulose	26	22	85.2
Sodium Carbonate	39	17	71.5
HPAN Grafted Fibers*	52	26	82.6

*The HPAN Grafted Fibers in the above example were prepared by polymerizing acrylonitrile on cellulose fibers according to the procedure of Example 1 to form a product having 220 parts of polyacrylonitrile per 100 parts of cellulose and then hydrolyzing the product according to the procedure of Example 3, followed by drying and ball milling the dry, hydrolyzed material to pass a 325 mesh screen.

It will be noted that the product of the present invention exhibited greater effectiveness than the commonly utilized building agents in the combined requirements of a builder in soil removal (percent Detergency) and in prevention of redeposition of soil (Brightness Retention of an Unsoiled Cloth). The washing composition containing carboxymethyl cellulose, which showed excellent brightness retention, nevertheless was seriously deificient from the standpoint of ability to remove soil (percent Detergency) whereas the builder of this invention was superior in both respects to both the phosphate and NTA (nitrilo triacetate) builders. When either of these latter materials is utilized as the major builder component of a detergent composition, it is necessary to also include 0.5 to 2 percent of carboxymethyl cellulose in the composition as an inhibitor to the redeposition of soil on the washed fabric. The inclusion of carboxymethyl cellulose is unnecessary in detergent compositions wherein HPAN grafted fibers are utilized as the builder component.

It has been previously mentioned that the ratio of grafted polymer to cellulose fiber may be varied within wide limits. The degree of polymer grafting on the cellulose fibers may be varied by varying the ratio of monomer to fiber in the reaction blend and also is affected by the type of wood fiber utilized as the host material. In general, between about 50 and 70 percent of the available monomer can be graft polymerized on a given fiber material, higher percentage conversions generally being obtained with unbleached fibers and preferably fibers of softwood origin. In the following example, polymer-grafted fibers containing amounts of polyacrylonitrile ranging from 35 parts to over 500 parts of polymer per 100 parts of fiber were prepared according to the procedure of Example 1, the monomer-to-fiber ratio being varied to give the various polymer-to-fiber ratios shown in the table.

The polymer-grafted fibers were subjected to an alkaline hydrolysis according to the procedure of Example 3, above, and the hydrolysis products were incorporated into wash waters used to wash standard test fabrics in the manner previously described.

EXAMPLE 7

Washing tests were carried out using 400 ppm hardness water containing 0.025 percent Tergitol 15-S-9 (a non-ionic surfactant obtainable from Union Carbide Corporation) and 0.15 percent of hydrolyzed polymer-grafted fibers prepared in the manner hereinbefore described. The results of the washing tests are shown in Table II, together with control tests in which test swatches were washed in plain hard water and in hard water containing only the surfactant with no builder additive.

TABLE II

WASHING TESTS USING VARYING RATIOS OF POLYMER-FIBER IN THE BUILDER

Polyacrylonitrile Concentration on 100 Parts of Fiber	% Detergency Testfabric Cloth	% Detergency U.S. Testing Cloth	Brightness of Unsoiled Cloth After Washing
Control-Hard Water Only	16	4	82
Control-Hard Water with Tergitol only-No Builder	20	20	68.2
35 parts/100 parts fiber	26	25	75.9
68 parts/100 parts fiber	30	26	77.5
105 parts/100 parts fiber	40	24	81.6
164 parts/100 parts fiber	31	28	80.2
179 parts/100 parts fiber	45	20	80.7
220 parts/100 parts fiber	50	23	82.4
268 parts/100 parts fiber	45	21	81.4
423 parts/100 parts fiber	46	22	80.5
523 parts/100 parts fiber	46	20	81.4

The tabulated results clearly indicate the usefulness of the product of this invention as a builder for detergents over a wide range of ratios of polymer-to-fiber in the product.

EXAMPLE 8

In order to illustrate the effect of various hydrolysis procedures and treatments of polymer-grafted fibers after hydrolysis, acrylonitrile was polymerized in and on wood cellulose pulp fibers in the ratio of 220 parts of polymers to 100 parts of pulp fibers. The product was separated and individual portions treated by the following hydrolysis procedures:

A. Hydrolysis carried out in a 5 percent slurry as disclosed in Example 2. The 5 percent slurry was used directly as a detergent builder.

B. Hydrolysis carried out in a 5 percent slurry as A, above, and the resulting slurry product was ball milled for 12 hours, the ball milled product then being used in slurry form as a detergent builder.

C. Hydrolysis carried out in a 5 percent slurry as in A, above, the reaction mass filtered and the fibrous product washed and then ball milled for 12 hours. The ball milled product was then used in slurry form as a detergent builder.

D. Hydrolysis carried out in a 5 percent slurry as in A, above, the product dried and ball milled to a fine powder, screened through 100 mesh standard screen, and the product used as a detergent builder.

E. The same treatment was in D, but the product was ball milled to pass a 200 mesh standard screen and then used as a detergent builder.

F. The same treatment as in D, but the product was ball milled to pass a 325 mesh standard screen and used as a detergent builder.

G. The polymer-grafted fibers were subjected to an alkaline hydrolysis in a 5 percent aqueous suspension, the excess alkali removed by addition of hydrochloric acid and the neutralized product dried and ball milled to pass a 325 mesh screen for use as a detergent builder.

H. The polymer-grafted fibers were hydrolyzed and acid treated as in G, above, the 50 parts of Na_2CO_3 were added per 100 parts of polymer-grafted fibers and the blend dried and ball milled to pass a 325 mesh screen as in Example 5 for use as a detergent builder.

I. The polymer-grafted fibers were hydrolyzed in a high solids reaction system as set forth in Example 4, above, and the product dried and ball milled to pass a 325 mesh screen for use as a detergent builder.

Washing tests were conducted in the manner previously described wherein the wash waters (400 ppm hardness) contained 0.025 percent of a non-ionic surfactant (Tergitol 15–S–9) and 0.15 percent (solids basis) of the builder of this invention processed in one of the manners described in A to I, above. The results of the washing tests are summarized in the following Table III.

TABLE III

EFFECT OF HYDROLYSIS PROCESSING VARIABLES ON THE DETERGENT BUILDER EFFICIENCY OF HYDROLYZED POLYMER-GRAFTED CELLULOSE FIBERS

Hydrolysis Procedure	% Detergency Testfabric Cloth	U.S. Testing Cloth	Brightness of Unsoiled Cloth After Washing
A.	39	19	83.9
B.	46	24	82.8
C.	39	22	82.7
D.	42	21	79
E.	39	22	79
F.	38	23	81.5
G.	35	21	78.3
H.	53	26	83.1
I.	41	28	83.4
Control-0.15% Sodium Tripolyphosphate	38	21	71.3

EXAMPLE 9

In order to further demonstrate the detergency effectiveness of the hydrolyzed polyacrylonitrile grafted cellulose fibers of this invention, washing tests were conducted in water of 400 ppm hardness containing (1) a surfactant alone, (2) polymerized and hydrolyzed acrylonitrile together with a surfactant, (3) the hydrolyzed polymer-grafted cellulose fibers alone, and finally (4) a surfactant together with the hydrolyzed polymer-grafted cellulose fibers. The results of the washing tests are tabulated in the following Table IV.

TABLE IV

WASHING TESTS OF VARIOUS CLEANING AGENTS

Cleaning Agent	% Detergency Testfabric Cloth	U.S. Testing Cloth	Brightness of Unsoiled Cloth After Washing
in 400 ppm Hardness Water			
Control - None	16	4	82
1. 0.025% Tergitol 15-S-9	20	20	68.2
2. 0.025% Tergitol 15-S-9 Plus 0.15% Hydrolyzed Polyacrylonitrile	40	16	76.8
3. 0.15% Hydrolyzed Polymer-Grafted Fibers (220 Parts Polymer to 100 Parts Fiber)	37	7	82.8
4. 0.025% Tergitol 15-S-9 Plus 0.15% Hydrolyzed Polymer-Grafted Fibers	50	23	82.4

It is evident from the data of Table IV that the hydrolyzed polymer-grafted fibrous material of this invention exhibits a high degree of building power in combination with a surfactant (see item 4 of Table IV) and also exhibits substantial cleaning power by itself (see item 3 of Table IV). Polyacrylonitrile formed by solution polymerization in the absence of cellulose fibers and subsequently hydrolyzed also shows some building power when combined with a surfactant (see item 2 in Table IV) but is less effective in this respect than is the hydrolyzed polymer-grafted fibrous product of this invention (see item 4 of Table IV).

Further washing tests indicate that the non-ionic surfactant used above (Tergitol 15–S–9) may be substituted by an anionic surfactant such as a linear alkyl benzene sulfonate or tallow alcohol sulfate with comparable results, thus demonstrating the effectiveness of the building agent of this invention in detergents containing either non-ionic or anionic surfactants. The builder of this invention is substantially ineffective in detergents having a cationic surfactant as a primary component.

EXAMPLE 10

100 parts of bleached Canadian softwood kraft wood pulp were slurried with 2,000 parts of a 0.2 percent ferrous sulfate solution for about 5 minutes at room temperature to fix ferrous ions on the cellulose fibers. After filtering and pressing to remove the excess ferrous sulfate solution, the pulp was dried at 105° C. for 30 minutes. The iron-treated pulp fibers were then slurried in a minute of 1,000 parts of methacrylic acid and 1,000 parts of distilled water and 10 parts of 30 percent hydrogen peroxide were added to the slurry. The slurry was then maintained in a sealed container for 18 hours at 38°–40° C., after which the reaction mass was neutralized by the addition of a strong (45 percent) aqueous solution of sodium hydroxide. The substantially neutral (pH = 6.0) suspension of cellulose fibers modified by the polymethacrylate salt grafted thereon was ball milled for 10 hours and then utilized as a builder ingredient by incorporating 0.15 percent (solids basis) therein together with 0.025 percent of Tergitol 15–S–9 in wash waters of 400 ppm hardness in washing tests conducted in the manner previously described. Results were similar to those obtained in tests utilizing HPAN grafted fibers as a building agent.

EXAMPLE 11

A satisfactory detergent builder according to this invention may be formed by polymerizing acrylonitrile in

the presence of cellulose fibers from any of a variety of sources including wood, straw, bagasse and the like and any of the common pulping processes, including kraft or sulfate pulping, bisulfite pulping, chemical and semi-chemical pulping. The fibers may be bleached or unbleached, although it has been found that polymer add-on is more readily obtained when unbleached pulp is used.

The following table contains data from washing tests using wash waters of 400 ppm hardness containing 0.025 percent of a non-ionic surfactant (Tergitol 15–S–9) and 0.15 percent of the hydrolyzed polymer-grafted cellulose fibers of this invention obtained from the particular wood sources and by the pulping procedures noted in the table. In each case, the polymerization of acrylonitrile on the fibers was carried out according to the procedure of Example 1 and the hydrolysis according to Example 3, above. Between 150 and 180 parts of polymer were formed for each 100 parts of fiber.

TABLE V

COMPARISON OF VARIOUS WOOD PULPS IN THE DETERGENT BUILDERS OF THIS INVENTION - WASHING TESTS - WASH WATERS OF 400 PPM HARDNESS CONTAINING 0.025% OF SURFACTANT AND 0.15% OF HPAN GRAFTED FIBERS

Wood Source	% Detergency Testfabric Cloth	U.S. Testing Cloth	Brightness of Unsoiled Cloth After Washing
Control - Surfactant Alone	20	20	68.2
Bleached Aspen and Birch, Kraft Pulp	31	28	81.6
Bleached Southern Pine, Kraft Pulp	30	26	80.4
Bleached Aspen, Sulfite Pulp	46	24	82.8

EXAMPLE 12

In order to compare the effectiveness of HPAN grafted fibers as a detergent builder in wash water of varying hardness when utilized with both anionic and non-ionic surfactants, test washings were conducted in wash waters of 50 ppm, 135 ppm and 300 ppm hardness, utilizing EMPA Standard Soiled Cotton Test Cloth obtained from Test-fabrics Incorporated, New York, New York as the fabric tested. The standard AHAM detergent obtained from the Association of Home Appliance Manufacturers was utilized as a control. In each case, the total detergent composition concentration utilized was 0.2 percent based on the total wash water.

The test detergent compositions were as follows:

1. Linear Alkyl Sulfonate	20 parts
Cocodiethanolamide (CDA)	2 parts
Sodium Silicate	6 parts
HPAN Grafted Fibers	20 parts
Water	52 parts
	100 parts
2. Tallow Alcohol Sulfate	20 parts
Cocodiethanolamide (CDA)	2 parts
Sodium Silicate	6 parts
HPAN Grafted Fibers	20 parts
Water	52 parts
	100 parts
3. Tergitol 15-S-9	9 parts
Sodium Silicate	6 parts
HPAN Grafted Fibers	20 parts
Water	65 parts
	100 parts

The results of the washing tests are contained in Table VI.

TABLE VI

DETERGENCY OF COMPOSITIONS CONTAINING HPAN GRAFTED FIBERS AND VARIOUS SURFACTANTS

Detergent Composition at 0.2% Conc.	% Detergency on EMPA Test Cloth Water Hardness 50 ppm	135 ppm	300 ppm
1. Linear Alkyl Sulfonate Formula	58	47	31
2. Tallow Alcohol Sulfate Formula	64	52	22
3. Tergitol Formula	60	43	29
4. Control - AHAM Standard Detergent	48	46	45

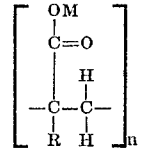
The above results demonstrate that the hydrolyzed, polymer-grafted fibers of the present invention are effective as a builder component in detergents based on both anionic and non-ionic surface active agents and that the resulting detergent compositions compare favorably with a standard detergent formula commonly used for test purposes in the industry.

It has previously been mentioned that the polymer-grafted fibrous products of this invention are insoluble in aqueous solutions. The use of this insoluble builder component in detergent solutions presents a unique ecological advantage over the phosphate and nitrilo triacetate components heretofore utilized for this purpose since the builders of this invention are removed from waste water streams in the customary primary sewage treatment as a portion of the sewage sludge. In fact, these materials have been found to contribute to the speed and efficiency of the sewage sludge formation by serving as a flocculation aid and a sediment conditioner. The sewage sludge therefore settles more quickly and the effluent stream does not contain the undesirable compounds normally resulting from the use of the customary water-soluble detergent builders.

Having now shown and described specific embodiments of the invention, it will be apparent that various modifications may be applied without departing from the spirit thereof and the invention is not intended to be restricted except in accordance with the spirit of the appended claims.

We claim:

1. A detergent composition consisting essentially of a detergent compound chosen from the group consisting of anionic and nonionic surface active detergent compounds and a water-insoluble, fibrous, hydrophilic building agent of natural cellulose fibers having chemically bonded therein and thereon by in situ formation a polymer of the general formula:



in which:

R is a hydrogen or a methyl group,

M is a sodium, potassium or ammonium ion, and

n is an integer greater than 500,

said polymer being present in an amount between about 50 and 500 parts by weight on each 100 parts of said cellulose fibers,

the weight ratio of said building agent to said detergent compound in said composition being between about 6 to 1 and about 1 to 1.

2. A detergent composition according to claim 1 wherein R is hydrogen.

3. A detergent composition according to claim 2 wherein said fibrous building agent is in the form of a finely divided powder.

4. A detergent composition according to claim 2 wherein said polymer comprises sodium polyacrylate.

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