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3,558,499

ANTI-REDEPOSITION AGENTS

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8 Claims

ABSTRACT OF THE DISCLOSURE

Built detergent compositions containing an anti-redeposition agent selected from the group consisting of graft copolymers of a polymerizable monomer and a water soluble or water dispersible polymeric material or a physical blend of a polymerized monomer and a water soluble or water dispersible polymeric material.

This is a continuation of Ser. No. 528,835, filed Feb. 21, 1966, now abandoned.

The present invention relates to detergent compositions and more particularly to built detergent compositions which contain a graft copolymer of a polymerizable vinyl monomer and a water soluble or water dispersible polymeric material as an anti-redeposition agent. Alternatively, the detergent compositions of this invention may contain a physical blend of a polymerized vinyl monomer and a water soluble or water dispersible polymeric material as an anti-redeposition agent.

Most modern detergent compositions contain not only a detergent compound but varying amounts of "builders," optical brighteners, perfumes and what are known as anti-redeposition agents. It is generally known that detergent compounds as such are effective in removing dirt from cloth but they do not have the colloidal character which acts to prevent redeposition of the dirt onto the cloth resulting in a dull, gray appearance. Therefore, in order to utilize the detergent materials effectively it is necessary to incorporate an anti-redeposition agent into the detergent composition along with the detergent compound, and "builders" in order to produce a satisfactory composition for washing purposes.

When incorporated in a detergent composition, the anti-redeposition agents act to keep the dirt, which is removed from the cloth during washing by the detergent compound, suspended in the wash water. By doing so, the suspended dirt will not become redeposited upon the washed cloth.

It is an object of this invention to provide a detergent composition which possesses anti-redeposition properties.

It is another object of this invention to provide a built detergent composition containing a graft copolymer of a polymerizable vinyl monomer and a water soluble or water dispersible polymeric material as an anti-redeposition agent.

It is a further object of this invention to provide a built detergent composition containing a blend of a polymerized vinyl monomer and a water soluble or water dispersible polymeric material as an anti-redeposition agent.

Other objects of the present invention will become apparent from the following description.

In accordance with the present invention graft copolymers of a polymerizable vinyl monomer and a water soluble or water dispersible polymeric material or a physical blend of a polymerized vinyl monomer and a water soluble or water dispersible polymeric material are incorporated in detergent compositions to impart anti-redeposition qualities therein. By the term "polymerizable

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vinyl monomer" as used herein is included vinyl monomers capable of free radical catalyzed polymerization.

In general, and in accordance with the present invention built detergent compositions contain (1) from about 10% to about 25% of a suitable detergent compound, (2) from about 60% to about 89.9% of "builders" and (3) from about 0.10% to about 10% of an anti-redeposition agent. As set forth above, such formulations may also contain minor amounts of perfume, and other suitable modifiers.

In the built detergent compositions of the present invention the detergent component may be anionic or nonionic. Among the anionic detergents that may be used are the sodium alkyl sulfonates, sodium alkyl sulfates, sodium alkyl aryl sulfonates, sodium salts of sulfated and sulfonated alkyl amides, sodium salts of sulfated and sulfonated esters, and the sodium salts of esters of polyhydric alcohol-sulfonates; however, any suitable anionic detergent may be used in the present composition. Examples of suitable anionic detergents are sodium long-chain hydrocarbon sulfonate (Alkanol 189-S, Du Pont, Wilmington, Del.), sodium lauryl sulfate (Dupanol C, Du Pont, Wilmington, Del.), sodium dodecylbenzene sulfonate (Ultrawet K, Atlantic Refining Co., Philadelphia, Pa.), sulfonated fatty amide (Pyrotex, Standard Chemical Products, Inc., Hoboken, N.J.), sulfonated fatty ester (Nopco 2272-R, Nopco Chemical Co., Newark, N.J.), sodium 1-(N-methyl-N-oleoyl-amino) ethyl sulfonate (Igepon T, General Aniline and Film Corp., New York, N.Y.).

Any suitable nonionic detergent may also be used in the present invention. Among the nonionic detergents that may be used in the present detergent compositions are condensation products of lower alkylene oxides, for example, ethylene oxide, propylene oxide, butylene oxides, and mixtures thereof, with compounds having at least one active hydrogen atom such as fatty acids, rosin acids, tall oil acids, alcohols, phenols, and alkyl phenols. Generally, these condensation products will have a mole ratio of alkylene oxide to the active hydrogen component of from about 8 to about 25 respectively. Examples of suitable nonionic detergents are dodecylphenol condensed with 15 moles of ethylene oxide; oleyl alcohol condensed with 15 moles of ethylene oxide, rosin acids condensed with 20 moles ethylene oxide, dodecanol condensed with 4 moles of propylene oxide plus 8 moles of ethylene oxide. Examples of commercially available nonionic detergents suitable for use according to the present invention are Renex 679 and Renex 690 (Atlas Chemical Industries, Inc., Wilmington, Del.), Tergitol 15-S-9 (Union Carbide Co.) and Standamul 18 (Standard Chemical Products).

Other types of nonionic detergents wherein the hydrophilic portion of the compound is supplied by polyhydric alcohols such as glycerol, sorbitol, mannitol, ethylene glycol, propylene glycol, erythritol and mixtures thereof may also be used in the present detergent composition.

The "builders" which are incorporated in the detergent compositions of this invention may be any of those which are generally used in known built detergent products. "Builders" as used in detergent compositions are used to enhance the activity of the detergent component. For example, borax, sodium carbonate, sodium tripolyphosphate, sodium metasilicate, sodium bicarbonate, sodium phosphate and tetrasodium pyrophosphate are commonly used as detergent builders and are suitable for inclusion in the products of the present invention.

The graft copolymers of a water soluble or water dispersible polymeric material and a polymerizable vinyl monomer which are utilized as anti-redeposition agents according to the present invention may be prepared by several different processes. Preferred processes are disclosed in U.S. patent application Ser. No. 258,119, filed

Feb. 13, 1963, now abandoned and U.S. patent application Ser. No. 33, 614, filed June 3, 1960, now abandoned and the entire disclosures thereof are hereby incorporated by reference. The process of application Ser. No. 258,119 comprises (1) contacting oxygen with a water-dispersible polymeric substrate while it is being irradiated whereby hydroperoxide groups are introduced into the said polymer and then (2) contacting the peroxidized polymeric substrate with an aqueous dispersion of a vinyl monomer capable of free radical induced polymerization in the presence of a catalyst capable of producing free radicals by reaction with hydroperoxides. The process disclosed in application Ser. No. 33,614 comprises moistening starch with water and then contacting the starch with a vinyl monomer in fluid form and then subjecting the resulting mixture to high energy radiation. However, other methods may be used to prepare suitable copolymers of a water soluble or water dispersible polymeric material and a polymerizable vinyl monomer such as those described in Great Britain Patent No. 869,329 and U.S. Pat. Nos. 2,999,056 and 2,998,329.

Among the starch products from which the copolymer anti-redeposition agents of this invention may be made are, for example, corn starch, tapioca starch, casein, amylose and sorghum. Additionally, any water soluble or water dispersible natural, modified natural products or synthetic polymers that can be radiation grafted by reactive monomers may be used. For example, casein, alginates, dextrin, dextran, polyvinyl alcohol polyvinylpyrrolidone, polyethylene glycol and methylcellulose may be used in preparing the anti-redeposition agents as used in the present invention.

The polymerizable vinyl monomers suitable for use in preparing the present graft copolymers may be suitably acrylic acid itself or methacrylic acid. The polyacrylic acid component of the anti-redeposition agent comprising a physical blend of a polymerized vinyl monomer and a water soluble or water dispersible polymeric material as used in the present invention may be polyacrylic acid itself or polymethacrylic acid. In general, it has been found that polyacrylic acid and polymethacrylic acid having a molecular weight in the range from about 5,000 to about 500,000 are suitable for use in the subject compositions.

It has been determined that a polyacrylic acid-starch graft copolymer suitable for use in the present invention will contain from about 1% to about 50% of a polyacrylic acid. However, it has been found that in most instances, polyacrylic acid starch grafts having from about 5% to about 40% of a polyacrylic acid content are preferred in view of excellent results obtained and economy. The above same concentrations are also applicable to present anti-redeposition agents made from an acrylic

acid and other suitable water dispersible or water soluble polymeric materials. The graft copolymers as used in this invention also include blends of grafts with sufficient water dispersible or water soluble polymeric materials to dilute the copolymer graft to the desired polyacrylic acid content.

It has been determined that physical blends (not grafted) of polymerized vinyl monomers and suitable water soluble or water dispersible polymeric material such as corn starch, potato starch, tapioca starch, amylose casein, sorghum, polyvinyl alcohol, methylcellulose, polyvinyl pyrrolidone and polyvinyl glycol may also be used as an anti-redeposition agent; however, such blends are not as effective as the grafted copolymer products. Such physical blends have a polyacrylic acid content in the same percentage range as the present polyacrylic acid-starch grafts.

The grafted copolymer anti-redeposition agents of this invention may also be used in the form of their salts. For example, the sodium, ammonium and potassium salts of polyacrylic acid-starch grafts copolymers are much more soluble in water than the polyacrylic acid-starch graft in its acid form and hence dissolved more rapidly in water than the acid form of the polyacrylic acid-starch graft copolymer. The salt of the polyacrylic acid-starch grafts can be readily prepared in several ways, for example, by adding sodium hydroxide, potassium hydroxide or ammonium hydroxide to an aqueous slurry of the polyacrylic acid starch graft copolymer until a pH of 7 is obtained and then precipitating the salt of the acid graft copolymer by pouring the neutralized solution into a lower alcohol such as methanol, ethanol or isopropanol.

In general, it has been found that from about 0.1% to about 10% of the subject anti-redeposition agents on the weight of a built detergent composition produce detergent products which exhibit excellent washing qualities. It is usually preferred to use from about 0.10% to about 5% of the present anti-redeposition agents on the basis of the built detergent composition due to economy and excellent results obtained. Concentrations less than 0.1% may be used but the anti-redeposition quality of the detergent composition is generally reduced; whereas with concentrations greater than 10% no significant improvement in anti-redeposition is obtained.

The anti-redeposition agents as disclosed in this invention may be incorporated in any suitable anionic or non-ionic detergent composition.

The following examples of detergent compositions of the present invention as set forth in Tables I and II will provide a further understanding of the products of this invention but is not limitative of the scope thereof. Unless otherwise indicated all parts and percentages indicated are by weight.

TABLE I

Example Number	Anti-redeposition agent composition									
	Sodium tripolyphosphate percent	Sodium metasilicate percent	Sodium carbonate percent	Renex 690 percent	Ultrawet K-Soft ² percent	PAA-PS ³ percent	PMAA-PS graft ⁴ percent	Potato starch	Acid content of anti-redeposition agent percent	Percent of anti-redeposition agent
1.....	34.82	9.95	39.81	14.92	-----	25	-----	75	10	0.50
2.....	34.65	9.90	39.60	14.85	-----	25	-----	75	10	1.00
3.....	34.47	9.86	39.40	14.77	-----	25	-----	75	10	1.50
4.....	34.92	9.98	39.89	14.96	-----	100	-----	-----	40	.25
5.....	34.82	9.95	39.81	14.92	-----	100	-----	-----	40	0.50
6.....	34.65	9.90	39.60	14.85	-----	100	-----	-----	40	1.00
7.....	34.65	9.90	39.60	14.85	-----	-----	25	75	10	1.00
8.....	34.92	9.98	39.89	14.96	-----	-----	100	-----	40	0.25
9.....	34.82	9.95	39.81	14.92	-----	-----	100	-----	40	0.50
10.....	34.65	9.90	39.60	14.85	-----	-----	100	-----	40	1.00
11.....	24.65	9.90	39.60	-----	14.85	25	-----	75	10	1.0
12.....	34.65	9.90	39.60	-----	14.85	10	-----	90	4	1.0
13.....	34.82	9.95	39.81	-----	14.92	-----	100	-----	40	0.50
14.....	34.65	9.90	39.60	-----	14.85	-----	100	-----	40	1.0
15.....	34.92	9.98	39.89	-----	14.96	100	-----	-----	40	0.25
16.....	34.82	9.95	39.81	-----	14.92	100	-----	-----	40	0.50
17.....	34.65	9.90	39.60	-----	14.85	100	-----	-----	40	1.00

¹ 10-polyoxyethylene nonylphenol (Atlas Chemical Industries, Inc.).

² Sodium dodecylbenzenesulfonate (Atlantic Refining Co.).

³ Polyacrylic Acid-potato starch graft.

⁴ Polymethacrylic acid-potato starch graft.

TABLE II

Example Number	Sodium tri-phosphate percent	Sodium metasilicate percent	Sodium carbonate percent	Renex 690 ¹ percent	Ultrawet K-Soft ² percent	Anti-redeposition agent	Percent anti-redeposition agent
18.....	35	10	39.5	15	-----	PAA ³	0.5
19.....	35	10	39.0	15	-----	PAA.....	1.0
20.....	35	10	39.5	15	-----	PAA-PVA ⁴ ..	0.5
21.....	35	10	39.0	15	-----	PAA-PVA.....	1.0
22.....	35	10	39.5	15	-----	PAA-MC ⁵	0.5
23.....	35	10	39.0	15	-----	PAA-MC.....	1.0
24.....	35	10	39.0	15	-----	25PAA/75PS ⁶	1.0
25.....	35	10	39.5	15	-----	25PAA/75PS..	0.5
26.....	35	10	39.0	15	-----	10PAA/90PS ⁷	1.0
27.....	35	10	39.0	-----	15	25PAA/75PS..	1.0
28.....	35	10	39.5	-----	15	25PAA/75PS..	0.5
29.....	35	10	39.0	-----	15	10PAA/90PS..	1.0

¹ 10-Polyoxyethylene nonylphenol (Atlas Chemical Industries, Inc.).

² Sodium dodecylbenzenesulfonate (Atlantic Refining Co.).

³ Polyacrylic acid, added in form of 25% aqueous solution (Acrysol A-3, Rohm and Haas, Washington Square).

⁴ Polyacrylic acid, polyvinyl alcohol graft (40% polyacrylic acid content).

⁵ Polyacrylic acid, methylecellulose graft (40% polyacrylic acid content).

⁶ Physical blend of 75% potato starch and 25% polyacrylic acid (added in form of Acrysol A-3).

⁷ Physical blend of 90% potato starch and 10% polyacrylic acid (added in form of Acrysol A-3).

The detergent compositions illustrated in Examples 1-29 above were tested for washing effectiveness and the results obtained are set forth in Table III below. A 0.25% concentration of each of the detergent compositions of Examples 1-29 and suitable control compositions were prepared in 1000 ml. of 300 p.p.m. hardness water, calculated as calcium carbonate of which the ratio of calcium to magnesium is 60/40. These detergent solutions were then used to wash four standard dirty cloths obtained from American Conditioning House, Boston, Massachusetts. A Baker Terg-O-Tometer (Baker Instrument Company, Orange, N.J.) was used for the tests. The Terg-O-Tometer was operated at 60 r.p.m. with the detergent bath water adjusted to 120° F. Each of the standard cloths were washed ten minutes, twice rinsed three minutes with 300 p.p.m. hardness water, (60/40 as Ca/Mg ratio calculated as CaCO₃) dried one hour at 185° F. and conditioned overnight at 75° C. at 40% relative humidity and then measured for changes in reflectance by the Hunter Multi-Purpose Reflectometer (Henry A. Gardner Laboratory, Inc., Washington, D.C.). The results obtained are expressed as percent increase in reflection of cloth after washing and percent efficiency of detergent composition based on a control as being 100%. Separate controls were run for each group of detergent compositions which were run at different times. Each control composition used in Group A, B, F, G and H was composed of the following detergent composition:

	Percent
Renex 690	15
Sodium tripolyphosphate	35
Sodium metasilicate	10
Sodium carbonate	40

The control compositions used in Groups C, D, E and I were composed of:

	Percent
Ultrawet K	15
Sodium tripolyphosphate	35
Sodium carbonate	10
Sodium metasilicate	40

TABLE III

Detergent example number	Percent increase in reflectance of soiled cloth after washing	Percent efficiency of detergent composition based on control of 100%
Group A:		
Control.....	72	100
1.....	81	111
2.....	80	110
3.....	90	124
4.....	92	126
5.....	89	123
6.....	90	125
Group B:		
Control.....	80	100
7.....	91	114
8.....	87	109
9.....	89	111
10.....	89	111

TABLE III.—Continued

Detergent example number	Percent increase in reflectance of soiled cloth after washing	Percent efficiency of detergent composition based on control of 100%
Group C:		
Control.....	121	100
11.....	132	109
12.....	126	104
Group D:		
Control.....	87	100
13.....	88	101
14.....	90	103
Group E:		
Control.....	125	100
15.....	128	102
16.....	133	106
17.....	134	107
Group F:		
Control.....	81	100
18.....	84	104
19.....	83	103
20.....	88	109
Group G:		
Control.....	79	100
21.....	88	111
22.....	85	107
23.....	85	108
Group H:		
Control.....	75	100
24.....	87	116
25.....	82	109
26.....	83	111
Group I:		
Control.....	85	100
27.....	90	106
28.....	91	109
29.....	90	105

What we claim is:

1. A detergent composition consisting essentially of:

(1) from about 10% to about 25% of organic synthetic detergent selected from the group consisting of organic synthetic anionic detergents and organic synthetic nonionic detergents,

(2) from about 60% to about 89.9% of inorganic detergent builders, and

(3) from about 0.1% to about 10% of an anti-redeposition agent which is a graft copolymer selected from the group consisting of graft copolymers of starch with acrylic acid, graft copolymers of starch with methacrylic acid, and the sodium, potassium and ammonium salts of the graft copolymers of starch with either acrylic acid or methacrylic acid, wherein the polymerized acrylic acid or methacrylic acid has a molecular weight from about 5,000 to 500,000 and is present, by weight of copolymer, in an amount of from about 1% to 50%.

2. A detergent composition of claim 1 wherein the polymerizable monomer is acrylic acid.

3. A detergent composition of claim 1 wherein the polymerizable monomer is methacrylic acid.

4. A detergent composition of claim 1 wherein the polymerizable monomer is a sodium, potassium, or ammonium salt of acrylic or methacrylic acid.

5. A detergent composition of claim 1 wherein the anti-

red deposition agent is a graft copolymer of potato starch and acrylic acid.

6. A detergent composition of claim 1 wherein the antiredeposition agent is a graft copolymer of potato starch and methacrylic acid.

7. A detergent composition of claim 1 wherein the detergent builders are selected from the group consisting of sodium tripolyphosphate, sodium metasilicate, sodium carbonate, borax, sodium bicarbonate, sodium phosphate, and tetrasodium pyrophosphate.

8. A detergent composition consisting essentially of:

(1) from about 10% to about 25% by weight of organic synthetic detergent selected from the group consisting of an organic synthetic anionic detergent and an organic synthetic nonionic detergent,

(2) from about 60% to about 89.9% by weight of inorganic detergent builders selected from the group consisting of sodium tripolyphosphate, sodium metasilicate, sodium carbonate, borax, sodium bicarbonate, sodium phosphate, and tetrasodium pyrophosphate, and

(3) from about 0.1% to about 10% by weight of an anti-red deposition agent which is a graft copolymer of potato starch and acrylic acid, said graft copolymer containing polymerized acrylic acid having a molecular weight from about 5,000 to about 500,000

and said graft copolymer containing from about 1% to about 50% by weight of polymerized acrylic acid.

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