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DETERGENT COMPOSITIONS FOR LAUNDERING TEXTILE FABRICS, CONTAINING A COPOLYMER OF A LOWER N-ALKYL ACRYLAMIDE AND VINYL ALCOHOL

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4 Claims. (Cl. 252—152)

This invention relates to detergent compositions for the laundering of textile fabrics. More particularly, it relates to detergent compositions which not only remove soil from textile fabrics, but prevent redeposition of the soil on the fabrics during the laundering operations.

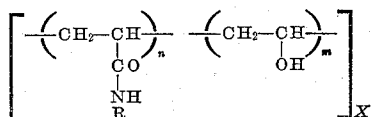
In the wet laundering of textile fabrics, the effectiveness of the detergency action is dependent upon two factors: removal of the soil from the fabric, and prevention of redeposition of the soil on the fabric before the laundering cycle is completed. Synthetic detergents are known to be excellent dispersing and cleaning agents; however, in the laundering of textile fabrics they are incapable of preventing a portion of the removed soil from redepositing on the fabric. In the case of dyed fabrics, the redeposited soil results in a considerable loss of the original brightness. In the case of white fabrics, it prevents restoration of their full whiteness.

A number of substances have been tested as adjuvants in detergent compositions, for preventing soil redeposition. Armstrong et al., American Dyestuff Reporter 37, 596 (1948), have compared polyvinyl alcohol, methyl cellulose, potato dextrin, chrome glue, cornstarch, bentonite, and sodium carboxymethylcellulose in their effectiveness for this purpose. With the exception of sodium carboxymethylcellulose, however, none of these substances has found general acceptance in the trade.

Although carboxymethylcellulose is moderately effective for preventing soil redeposition in the laundering of cotton fabrics, it suffers the disadvantage of being ionic in nature, and is readily precipitated by salts of di- and polyvalent metals such as calcium, magnesium, zinc, iron and aluminum. It is therefore adversely affected by hard water. Moreover, even in soft water, it does not prevent redeposition of soil in the laundering of cellulose acetate, nylon or wool.

We have discovered that the addition of copolymers of lower N-alkyl-acrylamides and vinyl alcohol to anionic or non-ionic detergents prevents redeposition of soil on textile fabrics when the fabrics are washed with these detergents. In the term "anionic detergents," we mean to include soap as well as the synthetic anionic detergents.

The copolymers of lower N-alkyl-acrylamides and vinyl alcohol have the general structure



The ratio of n to m lies in the range of 1:1 to 10:1; $X=50$ to 1000. R is a lower alkyl group. These copoly-

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mers are advantageously prepared from (emulsion) copolymers of a methacrylate and vinyl acetate. They may contain 30–80% of alkacrylate. Preferably, 40–60% of alkacrylate is employed. The copolymer of alkacrylate and vinyl acetate is heated with 2–5 parts of, for example, methyl, ethyl, or isopropyl alcohol containing 0.5–2 parts of an amine or ammonia ammonolysis reagent. The ammonolysis reaction preferably is carried out in a pressure vessel equipped with agitating means at 80–120° C. for 2–4 hours.

The copolymer of lower N-alkyl-acrylamide with vinyl alcohol derived by the ammonolysis procedure is isolated by evaporation of the solvent or by pouring the solution into a precipitant such as benzene or isopropyl ether. Suitable ammonolysis reagents include various amines such as monomethyl, monoethyl, mono-isopropyl, and monobutyl amines. Cyclic amines such as morpholine, piperidine, and pyrrolidine may also be employed. The lower aliphatic amines, however, are advantageous, since with them a high conversion to the corresponding N-alkyl-acrylamide is obtained. The conversion ordinarily is in the range of 50–90%, and the products in most cases are soluble in water.

The lower N-alkyl-acrylamide-vinyl alcohol copolymers may also be prepared by hydrolyzing the acetyl groups from lower N-alkyl-acrylamide-vinyl acetate interpolymers. For example, an interpolymer containing 75% N-isopropyl acrylamide-25% vinyl acetate may be selectively hydrolyzed by known methods, using dilute sulfuric acid, to remove the acetyl groups but leaving the N-isopropyl amide groups unchanged. The hydrolysis may be carried out in alcohol, water, or other suitable medium. Ammonium hydroxide or amines at 25–100° C. are especially suitable for the selective hydrolysis. Sodium carbonate or sodium hydroxide may be used. Interpolymers of vinyl acetate with the following amides may, for example, be used: N-methyl acrylamide, N-ethyl acrylamide, N-isopropyl acrylamide. The interpolymers may contain from 20 to 70% vinyl acetate, and preferably 40 to 60% vinyl acetate before hydrolysis.

Our novel detergent compositions are mixtures of copolymers of lower N-alkyl-acrylamides and vinyl alcohol, with a detergent selected from the group consisting of the anionic detergents, including soap, and the non-ionic detergents, in ratios ranging from 1 part copolymer:99 parts detergent to 25 parts copolymer:75 parts detergent. Although higher proportions of the copolymer can be used, the improvement in the cleaning power was found to reach a maximum at 25 parts copolymer:75 parts detergent. Improvement in detergency was noticeable at a ratio of 1 part copolymer:99 parts detergent. However, the most desirable range is from 2 parts copolymer:98 parts detergent to 10 parts copolymer:90 parts detergent.

Using the following types of detergents, we have found that a mixture of 95 parts by weight of detergent and 5 parts by weight of lower N-alkylacrylamide-vinyl alcohol copolymer gives better detergency than 100 parts by weight of the same detergent:

1. An alkyl sulfate (anionic)
2. An alkyl sulfonate (anionic)
3. An alkyl-aryl sulfonate (anionic)

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4. A sulfonated amide (anionic)
5. A fatty acid-polyethylene glycol condensate (non-ionic)
6. A phenol-polyethylene glycol condensate (non-ionic)
7. An alcohol-polyethylene glycol condensate (non-ionic)
8. A mercaptan-polyethylene glycol condensate (non-ionic)
9. A polypropylene glycol-polyethylene glycol condensate (non-ionic)
10. Soap (anionic)

The improvement obtained by the substitution of the lower N-alkylacrylamide-vinyl alcohol copolymers for a portion of a detergent (or detergent-builder combination) varies according to the efficiency of the original detergent formulation. For example, by means of these copolymers it is possible to improve anionic type synthetic detergents to the point where they are equal or superior to soap in their ability to prevent soil redeposition during the laundering of textile fabrics. These copolymers also improve soap alone or soap-alkaline builder formulations. In general, therefore, it can be said that by the substitution of these lower N-alkylacrylamide-vinyl alcohol copolymers for a small portion of a detergent formulation in which the detergent is selected from the group consisting of the anionic detergents, including soap, and the non-ionic detergents, a remarkable improvement is obtained in the ability of the detergent formulation to prevent soil redeposition.

The mechanism by which these copolymers function as detergent adjuvants is still to be determined. One possible explanation is that the copolymers are selectively adsorbed on the fabric, building a charge that repels the dirt particles after they have once been removed from the fabric. Another explanation is that the copolymers function as soil-suspending agents. Although these copolymers have soil-suspending properties, this mode of action cannot be considered to be the only explanation of their ability to prevent soil redeposition. A large number of water-soluble polymers are known to be excellent suspending agents, yet they do not possess the detergency properties exhibited by either sodium carboxymethylcellulose or the copolymers herein described. This is shown by the following example.

EXAMPLE 1

A detergent solution containing suspended carbon soil was prepared by dispersing 14 grams of Aquablak-B (a 35% aqueous suspension of carbon black, manufactured by Binney & Smith Company, New York, New York) in 11 liters of water containing 25 grams of Igepon T (a sulfonated amide, anionic type detergent, having the formula $C_{17}H_{33}CON(CH_3)C_2H_4SO_3Na$). Several 100-ml. portions of this stock solution were removed, and to all but one (control) of these portions there was added 0.0125 g. of a water-soluble polymer selected from the list shown in the table below. Thus the weight of adjuvant was approximately 5% of the weight of detergent, in each sample. The solutions were transferred to standard Launder-O-Meter bottles (pint size), each containing 10 steel balls, $\frac{1}{4}$ " in diameter. The bottles of detergent-soil solutions were preheated to 140° F., and a $2\frac{1}{2}$ " x $3\frac{1}{2}$ " piece of clean cotton broadcloth was placed in each bottle. The bottles were sealed and tumbled for 30 minutes at 140° F. in an Atlas Launder-O-Meter. The cloth samples were then removed from the soil solutions, rinsed in warm water, and dried. Reflectance curves were obtained for each washed cloth sample by means of a General Electric recording spectrophotometer. The average percent reflectance values were calculated for the curves. These values were then converted to "per-

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cent whiteness retained" by means of the following formula:

$$\text{Percent whiteness retained} = \frac{R_w}{R_o} \times 100$$

R_w = average reflectance of the cloth laundered in the soil solution

R_o = reflectance of the white broadcloth before laundering.

Table I shows the results of these tests.

Table I

[Detergent: Igepon T.]

Adjuvant	Percent Whiteness Retained by the Laundered Cloth
None.....	22
Sodium carboxymethylcellulose.....	61
66 N-Methylacrylamide-34 vinyl alcohol, copolymer.....	74
80 N-Methylacrylamide-20 vinyl alcohol, copolymer.....	82
Hydroxyethylcellulose (Cellosize).....	30
Methylcellulose (Methocel).....	31
Cornstarch.....	13
Dextrin.....	14
Pectin (citrus).....	49
Sodium alginate (Kelgin).....	9
Propylene glycol alginate (Kelcoioid).....	44
Locust bean gum.....	38
Mesquite gum.....	44
Gum arabic.....	45
Polyvinyl alcohol (Elvanol).....	24
Dextran (unhydrolyzed).....	20
Sodium salt of maleic acid-styrene copolymer (Sodium Stymer).....	12
Sodium polyacrylate.....	25
Polyvinyl pyrrolidone.....	17
Sodium salt of 50 maleic acid-50 isopropenyl acetate copolymer.....	25
70 Acrylic acid-30 acrylonitrile copolymer.....	18
Poly-N-isopropylacrylamide.....	35
Poly-N-isopropylmethacrylamide.....	31
72 N-Methylacrylamide-28 allyl alcohol copolymer.....	21
Bentonite.....	26

It will be seen that the lower N-alkyl-acrylamide-vinyl alcohol copolymers gave better results than any of the other adjuvants in preventing soil deposition, even giving improved results as compared to sodium carboxymethylcellulose.

The following example illustrates how three detergents are improved by substituting, for 5% of the detergent, copolymers of N-methylacrylamide-vinyl alcohol ($X=500$).

EXAMPLE 2

A series of detergent solutions were prepared, having the compositions shown in Table II, so that the total concentration of detergent formulation in each was 0.25%, and the adjuvant portion of the detergent formulation was 0.0125 g., or approximately 5% based on the detergent weight. In 100 ml. of each of the detergent solutions, a $2\frac{1}{2}$ " x $3\frac{1}{2}$ " swatch of standard soiled cotton broadcloth (P. S. C. soiled cotton, sold by Foster D. Snell, Inc., New York, N. Y.) was laundered for 30 minutes at 140° F., using an Atlas Launder-O-Meter and 10 steel abrasion balls. The laundered swatches were rinsed in distilled water at 140° F., and the laundering cycle was repeated. After three successive washings the laundered swatches were ironed and dried. Reflectance curves were then obtained for each cloth sample, using a General Electric recording spectrophotometer. This data was converted to "percent whiteness regained" values by means of the formula:

$$\text{Percent whiteness regained} = \frac{R_w - R_s}{R_o - R_s} \times 100$$

R_w = percent reflectance of the soiled swatch after washing
 R_s = percent reflectance of the soiled swatch before washing (27% $\pm$ 1%)

R_o = percent reflectance of the unsoiled swatch (86% $\pm$ 1.5%)

The results are shown in Table II.

Table II.—Soil removal—Cotton

Detergent Formulation (Grams dissolved material in 100 ml. distilled water)	Percent whiteness regained
0.25 g. Igepon T* (control).....	27
0.24 g. Igepon T+0.0125 g. Na-carboxymethyl cellulose.....	35
0.24 g. Igepon T+0.0125 g. 66 N-methyl-acrylamide—34 vinyl alcohol copolymer.....	37
0.24 g. Igepon T+0.0125 g. 80 N-methyl acrylamide—20 vinyl alcohol copolymer.....	38
0.25 g. Kreeleon 4D* (control).....	22
0.24 g. Kreeleon 4D+0.0125 g. Na-carboxy-methyl cellulose.....	32
0.24 g. Kreeleon 4D+0.0125 g. 66 N-methyl-acrylamide—34 vinyl alcohol copolymer.....	32
0.24 g. Kreeleon 4D+0.0125 g. 80 N-methyl-acrylamide—20 vinyl alcohol copolymer.....	31
0.25 g. Duponol ME* (control).....	29
0.24 g. Duponol ME+0.0125 g. Na-carboxy-methylcellulose.....	39
0.24 g. Duponol ME+0.0125 g. 66 N-methyl-acrylamide—34 vinyl alcohol copolymer.....	38
0.24 g. Duponol ME+0.0125 g. 80 N-methyl-acrylamide—20 vinyl alcohol copolymer.....	38
0.25 g. Ivory soap* (control).....	39
0.24 g. Ivory soap+0.0125 g. Na-carboxy-methylcellulose.....	48
0.24 g. Ivory soap+0.0125 g. 66 N-methyl-acrylamide—34 vinyl alcohol copolymer.....	49
0.24 g. Ivory soap+0.0125 g. 80 N-methyl-acrylamide—20 vinyl alcohol copolymer.....	50
0.25 g. Igepal CA* (control).....	30
0.24 g. Igepal CA+0.0125 g. Na-carboxy-methylcellulose.....	38
0.24 g. Igepal CA+0.0125 g. 66 N-methyl-acrylamide—34 vinyl alcohol copolymer.....	36
0.24 g. Igepal CA+0.0125 g. 80 N-methyl-acrylamide—20 vinyl alcohol copolymer.....	40

*Igepon T is a sulfonated amide, anionic type detergent, having the formula $C_{17}H_{35}CON(CH_3)C_8H_{17}SO_3Na$, manufactured by General Dyestuff Corp. Kreeleon 4D is a sodium alkylaryl sulfonate type anionic detergent, manufactured by the Wyandotte Chemicals Corp. Duponol ME is a fatty alcohol sulfate anionic detergent (technical sodium lauryl sulfate), manufactured by E. I. du Pont de Nemours & Co. Ivory Soap is a sodium soap of vegetable oil fatty acids, manufactured by Procter & Gamble. Igepal CA is a non-ionic polymerized ethylene oxide condensation product, manufactured by General Dyestuff Corp.

It will be seen that the N-alkylacrylamide-vinyl alcohol copolymers gave results equal to those given by sodium carboxymethyl cellulose, as to soil removal.

EXAMPLE 3. WHITENESS RETENTION TESTS

This example illustrates the ability of the copolymers of N-methylacrylamide-vinyl alcohol, in which $X=600$, to prevent wet soil deposition on cotton, nylon, cellulose acetate, and wool.

Clean $2\frac{1}{2}'' \times 3\frac{1}{2}''$ swatches of cotton, nylon, cellulose acetate, and wool were separately laundered in freshly prepared detergent-soil solutions as listed in Table III. Each solution contained 100 ml. water, 0.25 g. detergent, 0.14 g. Aquablak-B, and 0.0125 g. adjuvant (5% adjuvant based on the weight of detergent), with the exception of the control solutions, which contained no adjuvant. Only one laundering cycle was employed. This was carried out in an Atlas Launder-O-Meter at $110^\circ F.$, using the standard pint jars and 10 steel abrasion balls in each jar. After a 30-minute treatment, the swatches were removed and separately rinsed in clean water at $110^\circ F.$ When dry, the samples were ironed.

Reflectance values were obtained for each of the washed and ironed samples by means of a General Electric recording spectrophotometer. These values were substituted in the formula

$$\frac{R_w}{R_o} \times 100$$

to obtain the "percent whiteness retained" for each cloth sample. The results are shown in Table III.

Table III.—Whiteness retention—Cotton, nylon, cellulose acetate, wool

Detergent Solution (Grams dissolved material in 100 ml. water)	Fabric	Percent Whiteness Retained
0.25 g. Kreeleon 4D (Control).....	Cotton.....	24
Do.....	Nylon.....	11
Do.....	Cellulose acetate.....	24
Do.....	Wool.....	53
0.25 g. Kreeleon 4D+0.0125 g. Na-carboxy-methylcellulose.....	Cotton.....	64
Do.....	Nylon.....	12
Do.....	Cellulose acetate.....	30
Do.....	Wool.....	52
0.25 g. Kreeleon 4D+0.0125 g. 80 N-methylacrylamide—20 vinyl alcohol, copolymer.....	Cotton.....	85
Do.....	Nylon.....	45
Do.....	Cellulose acetate.....	87
Do.....	Wool.....	60
0.25 g. Naeconol NR* (Control).....	Cotton.....	22
Do.....	Nylon.....	12
Do.....	Cellulose acetate.....	28
Do.....	Wool.....	56
0.25 g. Naeconol NR+0.0125 g. Na-carboxymethylcellulose.....	Cotton.....	61
Do.....	Nylon.....	14
Do.....	Cellulose acetate.....	37
Do.....	Wool.....	53
0.25 g. Naeconol+0.0125 g. 80 N-methylacrylamide—20 vinyl alcohol, copolymer.....	Cotton.....	82
Do.....	Nylon.....	40
Do.....	Cellulose acetate.....	84
Do.....	Wool.....	66
0.25 g. Ivory soap (Control).....	Cotton.....	51
Do.....	Nylon.....	26
Do.....	Cellulose acetate.....	81
Do.....	Wool.....	70
0.25 g. Ivory soap+0.0125 g. Na-carboxy-methylcellulose.....	Cotton.....	68
Do.....	Nylon.....	30
Do.....	Cellulose acetate.....	81
Do.....	Wool.....	74
0.25 g. Ivory soap+0.0125 g. 80 N-methylacrylamide—20 vinyl alcohol copolymer.....	Cotton.....	92
Do.....	Nylon.....	84
Do.....	Cellulose acetate.....	85
Do.....	Wool.....	80

*Naeconol NR is an alkyl aryl sodium sulfonate anionic detergent manufactured by the National Aniline Division of the Allied Chemical & Dye Corp.

The nylon cloth used in this example was made of desized, delustered taffeta filament, and was obtained from Test Fabrics, Inc. The cellulose acetate cloth was broadcloth weight, made of plain spun staple. The wool cloth was broadcloth weight, plain weave, obtained from Test Fabrics, Inc. The cotton cloth was Indian Head domestic broadcloth.

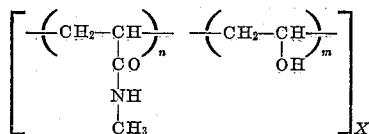
As Kreeleon and Naeconol are the same type of detergent, namely an alkyl aryl sodium sulfonate, it would be expected that similar results would be obtained with them, and it will be observed from Table III that this is the case. In the case of cotton, with the detergents, great improvement was brought about by the use of sodium carboxymethylcellulose, and even greater improvement by the use of the copolymer; with soap, some improvement was brought about by the use of sodium carboxymethylcellulose, and much greater improvement by the use of the copolymer. In the case of nylon, with the detergents, no improvement was brought about by the use of sodium carboxymethylcellulose, whereas considerable improvement was brought about by the use of the copolymer; with soap, a slight improvement was brought about by the use of sodium carboxymethyl cellulose, and a great improvement by the use of the copolymer. In the case of cellulose acetate, with the detergents, a slight improvement was brought about by the use of sodium carboxymethyl-cellulose, and a great improvement by the use of the copolymer; with soap, which gave good results in the control, there was little change when either adjuvant was used. In the case of wool, with the detergents, no improvement was given by the use of sodium carboxymethylcellulose, whereas some improvement was given by the use of the copolymer; with soap, which gave good results in the control, a slight improvement was given by

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the use of sodium carboxymethylcellulose, and somewhat more improvement was given by the use of the copolymer.

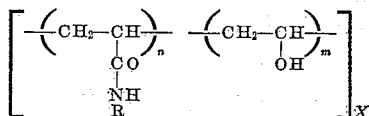
What we claim as our invention and desire to be secured by Letters Patent of the United States is:

1. A detergent composition comprising an organic anionic detergent and a copolymer of N-methylacrylamide and vinyl alcohol, the copolymer having the general structure



wherein the ratio of n to m lies in the range of 1:1 to 10:1, and $X=50$ to 1000, the ratio by weight of copolymer to detergent being in the range from 1:99 to 25:75.

2. A detergent composition comprising an organic anionic detergent and a copolymer of vinyl alcohol and a N-alkyl acrylamide in which the alkyl group contains from 1 to 3 carbon atoms, the copolymer having the general structure

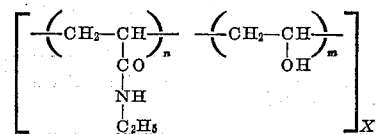


wherein the ratio of n to m lies in the range of 1:1 to 10:1, $X=50$ to 1000, and R is an alkyl group of from 1 to 3 carbon atoms, the ratio by weight of copolymer to detergent being in the range from 1:99 to 25:75.

3. A detergent composition comprising an organic anionic detergent and a copolymer of N-ethylacrylamide

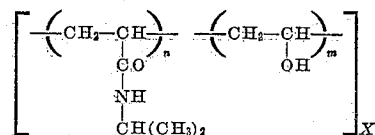
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and vinyl alcohol, the copolymer having the general structure



wherein the ratio of n to m lies in the range of 1:1 to 10:1, and $X=50$ to 1000, the ratio by weight of copolymer to detergent being in the range from 1:99 to 25:75.

4. A detergent composition comprising an organic anionic detergent and a copolymer of N-isopropylacrylamide and vinyl alcohol, the copolymer having the general structure



wherein the ratio of n to m lies in the range of 1:1 to 10:1, and $X=50$ to 1000, the ratio by weight of copolymer to detergent being in the range from 1:99 to 25:75.

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