

1
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DETERGENT COMPOSITIONS FOR LAUNDERING TEXTILE FABRICS, CONTAINING A COPOLYMER OF ACRYLONITRILE AND AN ACRYLAMIDE

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No Drawing. Application February 11, 1953,
Serial No. 336,442

3 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.

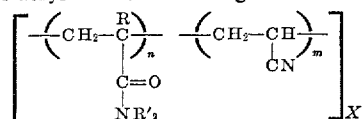
In the wet laundering of textile fabrics, the effectiveness of the detergency action is dependent upon two factors: removal of the soil from the fabric, and prevention of redeposition of the soil on the fabric before the laundering cycle is completed. Synthetic detergents are known to be excellent dispersing 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 disadvantages 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 acrylonitrile and an acrylamide selected from the group consisting of acrylamide and the lower alkyl acrylamides to anionic or nonionic 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 acrylonitrile and an acrylamide selected from the group consisting of acrylamide and the lower alkyl acrylamides have the general structure



The ratio of n to m lies in the range of 1:1 to 20:1; $X=50$ to 1000; $R'=H$, CH_3 , C_2H_5 , or C_3H_7 ; $R=H$, CH_3 or C_2H_5 .

These copolymers are conveniently made by the copolymerization of acrylonitrile and the acrylamide in bulk solution or emulsion. The usual polymerization catalysts or initiating agents are used, and certain so-called activating agents such as sodium bisulfite may be used in connection with the catalyst. For example, an interpolymer containing 70% acrylonitrile and 30% N-

2

methylmethacrylamide can be prepared by heating a solution of 7 parts of acrylonitrile, 3 parts of N-methylmethacrylamide, and 0.1 part of potassium persulfate in 40 parts of water at 50° C. for 24 hours. The resulting copolymer is obtained as a clear viscous solution. The polymer can be isolated from the water solution by the addition of a non-solvent or by the evaporation of the water solution.

Our novel detergent compositions are mixtures of copolymers of acrylonitrile and an acrylamide selected from the group consisting of acrylamide and the lower alkyl acrylamides, 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 an acrylonitrile-acrylamide 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)
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 acrylonitrile-acrylamide 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 acrylonitrile-acrylamide 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 do not possess the detergency properties exhibited by either sodium carboxy-

methylcellulose 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, N. Y.) 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 "percent 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
85 N-Methylmethacrylamide-15 acrylonitrile copolymer	67
90 N-Methylmethacrylamide-10 acrylonitrile copolymer	68
70 N-Methylmethacrylamide-30 acrylonitrile copolymer	50
Pectin (citrus)	49
Gum arabic	45
Mesquite gum	44
Propylene glycol alginate (Kelcoloid)	44
Locust bean gum	38
Poly-N-isopropylacrylamide	35
Poly-N-isopropylmethacrylamide	31
Methyl cellulose	31
Hydroxyethylcellulose	30
Sodium salt of polyacrylic acid	25
60 Maleic acid-50 isopropenyl acetate copolymer-Na salt	25
85 N-Isopropylacrylamide-20 N-methylacrylamide copolymer	25
Polyvinyl alcohol (Elvanol)	24
Poly-N-methylacrylamide	23
72 N-Methylacrylamide-28 allyl alcohol copolymer	21
Dextran (unhydrolyzed)	20
70 Acrylic acid-30 acrylonitrile copolymer-Na salt	18
Poly-N-Methylmethacrylamide	18
40 Acrylic acid-60 N-isopropylacrylamide copolymer-Na salt	17
Polyvinylpyrrolidone	17
Dextrin	14
Cornstarch	13
Maleic acid-styrene copolymer-Na salt (Sodium Stymer)	12
Sodium alginate (Kelgin)	9

It will be seen that the N-methylmethacrylamide-acrylonitrile copolymers gave results averaging as good as those given by sodium carboxymethylcellulose, and better than those given by any of the other adjuvants, in preventing soil deposition.

The following examples illustrates how three detergents

are improved by substituting, for 5% of the detergent, copolymers of N-methylmethacrylamide-acrylonitrile ($X=500$).

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 formulas:

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

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.]

Determined Formulation (Grams dissolved material in 100 ml. distilled water)	Percent Whiteness Regained
40 0.25 g. Igepon T* (control)	27
0.24 g. Igepon T+0.0125 g. carboxymethylcellulose-Na salt	35
0.24 g. Igepon T+0.0125 g. 70 N-methylmethacrylamide-30 acrylonitrile	37
0.24 g. Igepon T+0.0125 g. 85 N-methylmethacrylamide-15 acrylonitrile	39
0.24 g. Igepon T+0.0125 g. 90 N-methylmethacrylamide-10 acrylonitrile	39
45 0.25 g. Kreelon 4D* (control)	22
0.24 g. Kreelon 4D+0.0125 g. carboxymethylcellulose-Na salt	32
0.24 g. Kreelon 4D+0.0125 g. 70 N-methylmethacrylamide-30 acrylonitrile	32
0.24 g. Kreelon 4D+0.0125 g. 85 N-methylmethacrylamide-15 acrylonitrile	35
0.24 g. Kreelon 4D+0.0125 g. 90 N-methylmethacrylamide-10 acrylonitrile	34
50 0.24 g. Duponol ME* (control)	29
0.24 g. Duponol ME+0.0125 g. carboxymethylcellulose-Na salt	39
0.24 g. Duponol ME+0.0125 g. 70 N-methylmethacrylamide-30 acrylonitrile	37
0.24 g. Duponol ME+0.0125 g. 85 N-methylmethacrylamide-15 acrylonitrile	40
0.24 g. Duponol ME+0.0125 g. 90 N-methylmethacrylamide-10 acrylonitrile	41
55 0.25 g. Ivory soap* (control)	39
0.24 g. Ivory soap+0.0125 g. carboxymethylcellulose-Na salt	48
0.24 g. Ivory soap+0.0125 g. 70 N-methylmethacrylamide-30 acrylonitrile	47
0.24 g. Ivory soap+0.0125 g. 85 N-methylmethacrylamide-15 acrylonitrile	49
0.24 g. Ivory soap+0.0125 g. 90 N-methylmethacrylamide-10 acrylonitrile	50
60 0.25 g. Igepal CA* (control)	30
0.24 g. Igepal CA+0.0125 g. carboxymethylcellulose-Na salt	38
0.24 g. Igepal CA+0.0125 g. 70 N-methylmethacrylamide-30 acrylonitrile	36
0.24 g. Igepal CA+0.0125 g. 85 N-methylmethacrylamide-15 acrylonitrile	40
0.24 g. Igepal CA+0.0125 g. 90 N-methylmethacrylamide-10 acrylonitrile	30

*Igepon T is a sulfonated amide, anionic type detergent, having the formula $C_{17}H_{33}CON(CH_3)C_2H_4SO_3Na$, manufactured by General Dye-stuff Corp. Kreelon 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 (iso-octyl phenoxyethylene ethanol), manufactured by General Dyestuffs Corp.

It will be seen that the acrylamide-acrylonitrile 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-methyl methacrylamide-acrylonitrile, 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. Aquabla-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°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°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. Kreeelon 4D (control).....	Cotton.....	24
Do.....	Nylon.....	11
Do.....	Cellulose acetate.....	24
Do.....	Wool.....	53
0.25 g. Kreeelon 4D+0.0125 g. carboxymethylcellulose—Na salt.....	Cotton.....	64
Do.....	Nylon.....	12
Do.....	Cellulose acetate.....	30
Do.....	Wool.....	52
0.25 g. Kreeelon 4D+0.0125 g. 85 N-methylmethacrylamide—15 acrylonitrile.....	Cotton.....	67
Do.....	Nylon.....	66
Do.....	Cellulose acetate.....	75
Do.....	Wool.....	80
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. carboxymethylcellulose—Na salt.....	Cotton.....	61
Do.....	Nylon.....	14
Do.....	Cellulose acetate.....	37
Do.....	Wool.....	53
0.25 g. Naeconol NR+0.0125 g. 85 N-methylmethacrylamide—15 acrylonitrile.....	Cotton.....	60
Do.....	Nylon.....	85
Do.....	Cellulose acetate.....	75
Do.....	Wool.....	70
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. carboxymethylcellulose—Na salt.....	Cotton.....	68
Do.....	Nylon.....	30
Do.....	Cellulose acetate.....	81
Do.....	Wool.....	74
0.25 g. Ivory soap+0.0125 g. 85 N-methylmethacrylamide—15 acrylonitrile.....	Cotton.....	82
Do.....	Nylon.....	72
Do.....	Cellulose acetate.....	89
Do.....	Wool.....	88

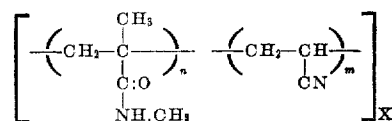
*Naeconol NR is an alkyl aryl sodium sulfonate anionic detergent manufactured by the National Aniline Division of the Allied Chemical & Dye Corp.

The nylon cloth used in this example was made of de-sized, 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 Kreeelon 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, except with nylon, where the copolymer gave considerably more improvement with Naeconol than with Kreeelon. In the case of cotton, with the detergents, great improvement was brought about by the use of carboxymethylcellulose, and approximately the same improvement by the use of the copolymer; with soap some improvement was brought about by the use of sodium carboxymethylcellulose, and greater improvement by the use of the copolymer. In the case of nylon, both with the detergents and with soap, no improvement was brought about by the use of sodium carboxymethylcellulose, whereas great improvement was brought about 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 carboxymethylcellulose, 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, both with the detergents and with soap, no improvement was given by the use of sodium carboxymethylcellulose, whereas moderate improvement was given by the use of the copolymer.

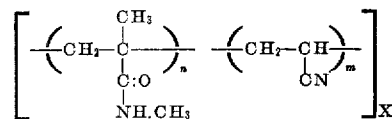
What we claim as our invention and desire to be secured by Letters Patent of the United States is:

1. A detergent composition comprising a detergent selected from the group consisting of the non-ionic detergents and the organic anionic detergents, and a copolymer of N-methylmethacrylamide and acrylonitrile, the copolymer having the structure



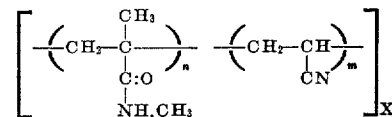
wherein the ratio of n to m lies in the range of 9:1 to 7:3, and $X=50$ to 1000, the ratio by weight of copolymer to detergent being in the range from 1:99 to 25:75.

2. A detergent composition comprising a non-ionic detergent and a copolymer of N-methylmethacrylamide and acrylonitrile, the copolymer having the structure



wherein the ratio of n to m lies in the range of 9:1 to 7:3, and $X=50$ to 1000, 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-methylmethacrylamide and acrylonitrile, the copolymer having the structure



2,805,205

7

wherein the ratio of n to m lies in the range of 9:1 to 7:3, and $X=50$ to 1000, the ratio by weight of copolymer to detergent being in the range from 1:99 to 25:75.

References Cited in the file of this patent

5

UNITED STATES PATENTS

2,486,241 Arnold ----- Oct. 25, 1949

8

FOREIGN PATENTS

950,645

France ----- Oct. 3, 1949