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(71) Applicant: **ROHM AND HAAS COMPANY**
Independence Mall West
Philadelphia, Pennsylvania 19195(US)

(72) Inventor: **Blankenship, Robert Mitchell**
914 St. Claire Lane
Harleysville, Pennsylvania 19438(US)
Inventor: **Morris, Hal Conley**
291 Magnolia Road
Warminster, Pennsylvania 18974(US)

(74) Representative: **Angell, David Whilton et al**
ROHM AND HAAS (UK) LTD. European
Operations Patent Department Lennig House
2 Mason's Avenue
Croydon CR9 3NB(GB)

(54) **High molecular weight acrylic polymers.**

(57) A polymer which is a copolymer of about 1-20 weight percent acrylic acid and about 80-99 weight percent methacrylic acid having a weight average molecular weight of from 80,000 to 350,000 is useful in improving the stain-resistance of fibre.

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HIGH MOLECULAR WEIGHT ACRYLIC POLYMERS

The present invention concerns polymers which are suitable for use in improving the stain-resistance of fiber. More particularly the invention concerns high molecular weight acrylic copolymers, the use of such copolymers for improving the stain resistance of fiber, a fiber comprising such copolymers and a method of treating fiber with such copolymers, a carpet comprising such copolymers and a method of treating carpet with such copolymers, and an anti-stain composition comprising such copolymers.

Nylon carpeting makes up a large percentage of the carpet industry. Nylon 66 fiber and nylon 6 fiber are used in carpets. Nylon 66 is more crystalline than nylon 6, thus limiting the depth of shade developed during dyeing of nylon 66 as well as beneficially limiting its staining. Conversely, with nylon 6 an advantageous depth of shade is possible; however, nylon 6 suffers from the drawback that known stain-resistant treatments are less effective on the fibers.

Known stain-resistant treatments for carpets containing nylon fiber include sulfonated naphthol/phenol formaldehyde condensates and dihydroxy diphenyl sulfones. However, in treating fibers made of nylon 6, relatively high levels of known stain-resistance materials are required. This imparts a stiffer hand to the fiber and, despite the increased level, the materials are more easily removed during shampooing in the carpet.

Furthermore, the known naphthol/phenol condensates and sulfone compounds, which act as clear dyes, have significant disadvantages. Both materials alter the color of the treated carpet yarn, especially on nylon 6 where higher levels are required. Additionally, the known materials yellow significantly when exposed to ultraviolet (UV) light, and are of questionable ecological safety.

A stain-resistant treatment using a blend of a methacrylic acid oligomer with a graft copolymer of methacrylic acid and sulfonated castor oil has been found to have an advantage over the phenolics and sulfones in color stability.

An object of the present invention is to develop an effective, durable stain-resistant treatment for fiber, particularly nylon fiber.

A further object of this invention is to provide an improved stain-resistant material for carpet, particularly nylon carpet, which conforms with current carpet manufacturing processes.

According to the present invention there is provided an anti-stain agent for carpet, preferably nylon carpet, and an improved method for treating fiber, preferably nylon fiber, with an anti-stain agent, wherein the agent comprises a water-soluble copolymer of from about 1 to about 20 weight percent acrylic acid and about 80 to about 99 weight percent methacrylic acid, and preferably from about 5-15 weight percent acrylic acid and about 85-95 weight percent methacrylic acid, that has a weight average molecular weight (MW) between about 80,000 and 350,000, preferably between about 100,000 and 250,000, more preferably between about 130,000 and 200,000, as determined by aqueous gel permeation chromatography (GPC). The upper limitation on the weight average molecular weight of the copolymer which functions in the practice of the present invention is determined by the water solubility, viscosity and practical process-of-manufacture requirements.

The present invention also provides a fiber impregnated with the anti-stain agent. Optionally, the anti-stain agent of the present invention can be combined with an adjuvant, such as a surfactant, novolac resin, ultraviolet-light absorber, organic or inorganic acid, antioxidant, ethoxylated or sulfonated fatty acid, polymer coating, or a mixture thereof.

The anti-stain agent of the present invention is useful in treating fiber materials, eg, fibers made from nylon and or amide fiber, preferably fiber used in the manufacture of carpets, to make them stain-resistant. Preferably, the fiber used in accordance with the present invention is made from nylon 6, which is a polymer of caprolactam, or nylon 66, which is a condensation product of adipic acid and hexamethylenediamine, which are well known in the manufacture of carpets such as disclosed in US Patent Nos. 4,501,591 and 4,780,499, the disclosures of which are incorporated herein by reference. Other useful nylon fibers include those made from, eg, nylon 11, which is a polymer of 11-amino undecanoic acid, nylon 610, which is a polycondensation product of sebacic acid and hexamethylenediamine, and a copolymer of nylon 6/nylon 66, all of which are well known as disclosed in the aforesaid US Patent No. 4,501,591.

Preferably, fiber is treated in accordance with the present invention by immersion in an acidic aqueous bath having a pH between about 1.5 and 5.5, preferably between 2.1 and 4.0, more preferably between 2.5 and 3.5, containing the anti-stain agent, which is maintained at a preferable temperature between about 38 and 110 °C, more preferably between about 80 and 100 °C. To obtain the best anti-stain effect, immersion time varies between about 1 and 20 minutes, more preferably between about 5 and 15 minutes, most preferably between about 7 and 12 minutes. The amount of anti-stain agent used in the bath varies between about 0.8 and 10 weight percent of the fiber to be treated, preferably between about 1.0 and 4.0 weight

percent, more preferably between about 1.2 and 3.0 weight percent. Acidity of the aqueous bath in combination with elevated temperature is maintained to assure optimum absorption by the fiber, this is particularly so when nylon fiber is treated. Acids useful in maintaining the proper pH include both organic and inorganic acids, eg, acetic acid, sulfamic acid, citric acid, nitric acid, formic acid and phosphoric acid, which are added in sufficient amount to maintain the pH in the preferred range. A surfactant is preferably added to the bath to assist in wetting the fiber at an amount between about 0.8 and 1.5 weight percent of the fiber to be treated. Useful surfactants include non-ionic and anionic surfactants, eg, sodium sulfosuccinate, dioctyl and dinonyl sulfosuccinates, nonyl phenol ethoxalates, linear-alkyl sulfonates and dodecylbenzene sulfonic acids. Other preferable additives, which may be introduced into the bath at between about 1 and 3 weight percent of the fiber to be treated, include anionic-acid dye levelers, novolac resins, such as sulfonated naphthol/phenol formaldehyde condensates and dihydroxydiphenyl sulfones; ultraviolet-light absorbers, eg, benzophenones, such as 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid, disodium-2,2'-dihydroxy-4,4'-dimethoxy-5,5'-disulfobenzophenone, 2,2', 4,4'- tetrahydroxybenzophenone, 2,4-dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, and 2,2'-dihydroxy-4,4'-dimethoxybenzophenone; antioxidants, such as sodium thiocyanate; ethoxylated or sulfonated fatty acids, eg, coconut oil, tall oil, castor oil, soybean oil and peanut oil; and polymeric coating compounds, eg, polyvinylchloride, polyvinylacetate, polyvinylalcohol, acrylics, styrenes, and fluorochemical compounds such as trifluoroethane. Fiber treated with the anti-stain agent may be used in the manufacture of carpet and cloth, eg, for furnishings (curtains, furniture coverings, etc) or clothes, though this list is not intended to be limiting on the potential use of the fiber.

A typical carpet process preferably involves first dyeing the carpet to a desired color, then saturating the carpet in the bath containing the anti-stain agent. Dyeing, however, can be performed after, or simultaneously with, the stain-resistant treatment. In treating carpets in accordance with the present invention a commercially available dyeing unit, such as available from the Oting Company or Kuster Corporation, is advantageously used. Such units and their operation are well known as disclosed in the aforesaid US Patent No.4,501,591.

A preferred processing system for treating carpet is described. The carpet is first wetted, for example with a solution containing by weight 0.2% Triton™ GR-5M (Rohm & Haas) and 0.1% TEA (Triethanolamine). After next passing through nip rolls, the carpet then is spray-dyed, steamed and rinsed. The stain-resist treatment is applied in the next stage, at conditions of about 160-180 °F/4 sec. (70-80 °C/4 sec.) using a Kuster unit. The carpet is thereafter steamed at, eg, 205 °F/120 sec. (90 °C/120 sec.) and rinsed. The carpet may be passed through a final spray for treatment with, eg, fluorocarbon.

In treating fiber in accordance with the present invention the fiber is impregnated with a sufficient amount of the anti-stain agent to impart stain resistance to the fiber. Preferably, the amount of anti-stain agent impregnated into the fiber varies between about 0.2 and 10.0 weight percent of the fiber, more preferably between about 0.2 and 1.0 weight percent, most preferably between about 0.3 and 0.75 weight percent.

resistance to a variety of materials, such as foods and beverages. Many such materials contain dyes, such as Food, Drug and Cosmetic (FD&C) Red Dye 40, that commonly come into contact with carpets when such products are accidentally spilled on the carpet. However, such dyes are easily removed from fiber carpets treated in accordance with the present invention by simple rinsing with water or using an aqueous solution of a mild, anionic, carpet shampoo. Rinse water temperatures are preferably maintained at about 15-65 °C, more preferably at about 26-38 °C.

In another aspect, the present invention provides an anti-stain composition comprising the copolymer and, optionally, a diluent or carrier for copolymer.

For all aspects of the present invention, nylon is the preferred fiber.

To more clearly describe the present invention, the following non-limiting examples are provided. In the examples, all parts and percentages are by weight unless indicated otherwise. In the examples, MW denotes weight average molecular weight determined by aqueous GPC, Mn denotes number average molecular weight, and MW/Mn denotes the molecular weight distribution.

EXAMPLE 1

Anti-stain agents according to the present invention were prepared as follows:

Two thousand grams of DI (deionized) water and 9g of 0.2% iron sulfate were added to a 5-liter 4-necked flask fitted with a stirrer, condenser and nitrogen inlet. This solution was heated under a nitrogen atmosphere to 7 °C.

A solution of 12.3g of SMBS (sodium metabisulfite) in 22.88g of DI water was prepared. 17.59g (50 weight percent) of this solution was then added to the flask (1% SMBS based on total monomer). To the flask were gradually and separately added the following feeds over 1.5 hours: 70g of AA (acrylic acid) and 530g of MAA (methacrylic acid); 0.9g sodium persulfate in 72g DI water, and the remainder of the SMBS/DI water solution (1% SMBS 72g DI water, and the remainder of the SMBS/DI water solution (1% SMBS on total monomer), while maintaining the temperature of the flask contents at 70 °C. The polymerized reaction was continued for 15 minutes after all the above feeds were completed. At this time was added 18g of 30% H₂O₂. Fifteen minutes later, 1379g of DI water was added. The flask was then allowed to cool to room temperature. The copolymer so formed (Sample 1) had an MW of 197,000, Mn of 29,700 and MW/Mn of 6.61.

The MW of the copolymer samples was varied by repeating the above process and varying the amount of SMBS and the ratio between the initial charge (to the flask/kettle) and the amount (remainder) used as co-feed. A copolymer (Sample 2) with MW = 201,000, Mn 27,300 and MW/Mn = 7.38 was obtained using 0.5% SMBS on total monomer in the kettle (in flask initially) with 1.5% SMBS on total monomer as co-feed. At 0.6% kettle SMBS and 1.22% co-fed SMBS on total monomer, a copolymer (Sample 3) with MW = 217,000, Mn = 29,000 and MW/Mn = 29,000 resulted; at 0.75% kettle SMBS and 2.25 co-fed SMBS on total monomer, a copolymer (Sample 4) with MW = 94,800, Mn = 24,000 and MW/Mn = 3.95 was obtained; and at 0.33% kettle SMBS and 0.33% co-fed SMBS on total monomer, a copolymer (Sample 5) with MW = 231,000, Mn = 47,100 and MW/Mn = 4.9 was produced.

EXAMPLE 2

Anti-stain agents according to the present invention were also produced by the following process:

To a 5-liter 4-necked flask was added 3000g DI water, which was heated to 85 °C under N₂. Nine grams of sodium persulfate (1.5 weight percent based on total monomer) in 320g DI water was then added. After two minutes, a mixture of 60g AA and 540g MAA was fed over a period of one hour to the flask, maintaining the temperature at 85 °C, after which 1035g of DI water was added. The flask was allowed to cool to room temperature. The MW of the resulting copolymer (Sample 6) was 84,000, the Mn was 26,300 and MW/Mn was 3.1.

Additional copolymers were also prepared by this method, by varying monomer, a copolymer (Sample 7) resulted having MW = 124,000, Mn = 38,400 and MW/Mn = 3.22.

EXAMPLE 3

As in Example 1, a co-feed of monomer and catalyst was used.

The catalyst solution added initially to the heated reactor flask was 1.5g sodium persulfate in 30g DI water (0.25 weight percent on total monomer).

The co-feed was 4.5g Na₂S₂O₈ in 100g DI water plus 60g AA and 1540g MAA. The co-feeds were added separately over one hour. The temperature was held at 93 °C for thirty minutes, and then 9g of 0.15% iron sulfate solution and 0.8g of t-butylhydroperoxide in 5g of DI water were added. Then, 1.2g of iso-ascorbic acid (IA) in 25g DI water was added. Ten minutes later, a second identical amount of IA/DI water was added. Next, 1035g DI water was added and the reaction flask was then allowed to cool to room temperature. The resulting copolymer (Sample 8) had an MW = 86,400.

The above process was repeated under the same conditions, except for the co-feeding time and the initial and co-fed percentages of sodium persulfate based on total monomer:

Sample 9: 0.167% sodium persulfate (based on total monomer) was added initially to the flask, with 0.503% co-fed. The molecular weight of the resulting copolymer was MW = 127,000.

Sample 10: Utilizing sodium persulfate as in Sample 10, with the co-feed time increased from 1 to 1.25 hours, yielded a copolymer with MW = 128,000.

Sample 11: Utilizing sodium persulfate in amounts as set forth in Sample 10, but with the co-feed time decreased from 1 to 0.75 hours, a copolymer was obtained with MW = 135,000.

Sample 12: 0.125% sodium persulfate was initially in the flask, and 0.375% sodium persulfate was co-fed. The copolymer produced had an MW = 157,000.

EXAMPLE 4

Carpet samples treated in accordance with the present invention were tested for durability and stain resistance in comparison with an untreated, unstained control and a stained, untreated control. The carpet samples tested were made of undyed, heat-set nylon 6 fiber.

A treatment bath was prepared containing 1201 parts deionized water, 1.25 parts sodium sulfosuccinate as a surfactant (available from Rohm and Haas Company under the name Triton™ GR-5M), 2.5 parts acetic acid, and 45 parts of a 1% solids aqueous solution of an anti-stain agent of the present invention. To treat a carpet sample, the bath was brought to a boil and then the sample was added to the bath and boiled for about ten minutes. After boiling, the sample was centrifuged and then dried at about 116° C for about 8-10 minutes.

The treated sample was shampooed to demonstrate the durability of the anti-stain treatment. This was performed by dipping the sample into a 2.11% aqueous solution of a carpet shampoo containing ethylenediaminetetraacetic acid tetrasodium salt (available from Blue Luster Home Care Products, Inc, Indianapolis, under the name Rinse 'n Vac™) at about 82° C for about 15 seconds, followed by rinsing the sample in cold water, centrifuging the sample, and then drying the sample at about 100° C for about 30 minutes.

The treated and control samples were then stained by immersion in a 10% aqueous solution of a food product containing citric acid and about 0.1% Food, Drug and Cosmetic Basic Red No.40 dye (cherry Kool-Aid™) for about five minutes at a temperature of about 41° C, followed by rinsing in cold water. The samples were then centrifuged followed by drying at 82° C.

The samples were evaluated for staining, by testing for brightness (on a scale of 1-50) using a Brightimeter Model 54-M Brightness Tester (Technidyne Corp). During the brightness measurements, the nap of the carpet was laid in the same direction for each carpet sample. Five brightness measurements were taken for each sample (2" x 2").

The results of the testing of the samples treated with anti-stain agents prepared according to Example 1 are given in Table 1 below:

TABLE 1

	Brightness (Standard deviation)		
<u>Sample</u>	<u>Unstained</u>	<u>Stained</u>	<u>Shampoo & Stained</u>
1	48.8 (2.9)	36.1 (2.1)	12.1 (2.3)
2		44.7 (5.3)	14.5 (0.7)
3		41.4 (4.6)	16.4 (1.2)
4		42.8 (1.2)	16.3 (2.6)
5		40.4 (3.5)	17.3 (2.7)
Control A*	48.8 (2.9)	1.6 (0.6)	
Control B*			
Both Control A and Control B were untreated.			

EXAMPLE 5

The procedures of Example 4 were repeated using the anti-stain agents prepared in accordance with Examples 2 and 3. The results are shown in Table 2 below.

TABLE 2

Sample	Brightness		
	Unstained	Stained	Shampoo & Stained
6		36.4	18.1
7		36.0	17.1
8		23.22	7.72
9		23.24	12.01
10		32.73	12.63
11		30.97	13.90
12		31.47	13.33
Control C*	48.8		
Control D*		1.6	
Both Control C and Control D were untreated.			

The tabulated results given in Examples 4 and 5 show the excellent stain resistance and durability of stain resistance of carpets treated in accordance with the present invention.

EXAMPLE 6

The procedure of Example 4 was repeated using an anti-stain agent prepared according to Example 3 having a weight average molecular weight of 135,000, except a commercial acid shampoo was utilized in place of "Rinse 'n Vac" (alkaline shampoo) in the last sample. The acid shampoo formulation was 35% butyl acrylate/15% styrene/50% methacrylic acid, neutralized with ammonia and catalyzed with zinc. The results are set forth in Table 3 below:

TABLE 3

Sample	Brightness
Treated Control (no shampoo/stained)	46.4
Alkaline Shampoo (stained)	16.2
Acid Shampoo (stained)	33.5

The results of this example demonstrate the durability of the carpet after treatment according to the invention, comparing a control sample with no shampoo step with samples that have been shampooed using standard alkaline and acid shampoos.

Claims

1. A polymer, suitable for use in improving the stain-resistance of fibre, which is a water-soluble copolymer of 1-20 weight percent acrylic acid and 80-99 weight percent methacrylic acid having a weight average molecular weight of from 80,000 to 350,000.
2. An anti-stain composition, suitable for improving the stain-resistance of fibre, comprising polymer as claimed in Claim 1 and, optionally, a diluent or carrier for the polymer.
3. Use of a polymer as claimed in Claim 1 or a composition as claimed in Claim 2 for improving the stain-resistance of fibre.
4. A fibre comprising polymer as claimed in Claim 1.
5. A method of manufacturing a fibre as claimed in Claim 4, which method comprises coating and/or

impregnating said fibre with said polymer.

6. A method as claimed in Claim 5, wherein said fibre is contacted with, eg, by immersion in a bath, an aqueous composition, comprising said polymer, in an amount of 0.8 to 10 weight percent based on the weight of fibre to be treated, having a pH of from 1.5 to 5.5.

5 7. A method as claimed in Claim 6, wherein the aqueous composition is at elevated temperature, preferably at a temperature of from 38 to 110 ° C.

8. A carpet comprising polymer as claimed in Claim 1.

9. A method of manufacturing a carpet as claimed in Claim 8, which method comprises applying, preferably at a temperature of 70-85 ° C, said polymer, optionally in the form of an anti-stain composition as claimed in

10 Claim 2, to said carpet.

10 10. A method as claimed in Claim 9, wherein the carpet is initially pretreated by wetting, nip rolling, spray-dyeing, steaming and/or rinsing, before the polymer is applied and, after the polymer is applied, the carpet is posttreated by steaming and, optionally, treating with fluorocarbon.

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