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54 **Maleic anhydride/olefin polymer stain resists.**

57 A polyamide fibrous substrate having deposited on it an amount of a composition effective to impart stain-resistance comprising a water-soluble or water-dispersible alpha-olefin/maleic anhydride polymer or a mixture of said polymers, and processes for preparing the substrates. The maleic anhydride polymer is used either in hydrolyzed form or in the form resulting from reacting it with a lower alkyl alcohol so as to form an alpha-olefin/maleic acid monoalkyl ester polymer

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FIELD OF THE INVENTION

The present invention relates to polyamide textile substrates treated with stain-resistant compositions comprising water-soluble or water-dispersible maleic anhydride/ alpha-olefin polymers, and processes for their synthesis. The substrates of this invention possess stain-resistance but do not suffer from yellowing to the extent that some previously known materials do.

BACKGROUND OF THE INVENTION

Polyamide substrates, such as nylon carpeting, upholstery fabric and the like, are subject to staining by a variety of agents, e.g., foods and beverages. An especially troublesome staining agent is FD&C Red Dye No. 40, commonly found in soft drink preparations. Different types of treatments have been proposed to deal with staining problems. One approach is to apply a highly fluorinated polymer to the substrate. Another is to use a composition containing a sulfonated phenol-formaldehyde condensation product.

For example, Liss et al., in U.S. Patent No. 4,963,409, disclose stain-resistant synthetic polyamide textile substrates having deposited on them sulfonated phenol-formaldehyde polymeric condensation products. However, sulfonated phenol-formaldehyde condensation products are themselves subject to discoloration; commonly they turn yellow. Yellowing problems are described by W. H. Hemmpel in a March 19, 1982 article in *America's Textiles*, entitled *Reversible Yellowing Not Finisher's Fault*. Hemmpel attributes yellowing to exposure of a phenol-based finish to nitrogen oxides and/or ultraviolet radiation. To deal with the yellowing problem, the condensation products were modified by Liss et al. by acylation or etherification of some of the phenolic hydroxyls. In a preferred embodiment disclosed by Liss et al., the modified condensation products were dissolved in a hydroxy-containing solvent, such as ethylene glycol prior to there being applied to the textile substrate.

Allen et al., in U.S. Patent 3,835,071, disclose rug shampoo compositions which upon drying leave very brittle, non-tacky residues which are easily removed when dry. The compositions comprise water-soluble metal, ammonium or amine salt of a styrene-maleic anhydride copolymer, or its half ester, and a detergent. Water-soluble metal salts of Group II and the alkali metals (particularly magnesium and sodium) are preferred and ammonium salts are most preferred by Allen et al.

On the other hand, Fitzgerald et al., in EP-A 0 329 899, disclose the usefulness of aqueous solutions of hydrolyzed vinylaromatic/maleic anhydride copolymers in the treatment of textiles to render them resistant to staining. The preferred copolymer of Fitzgerald et al. is a hydrolyzed styrene/maleic anhydride copolymer. Fitzgerald et al. disclose that the monoalkyl ester of their maleic anhydride/vinyl aromatic polymer was ineffective as a stain-resist.

Maleic anhydride/alpha-olefin polymers are known. EP-A 306,992 published 15 March 1989 discloses maleic anhydride/-1-alkene (C_4 - $_{30}$) polymers. Florjanczyk et al. in *Terpolymerization of Maleic Anhydride With Vinyl Monomers*, *J. Polymer Sci., Part A: Polym. Chem.*, 27 (12), 4099-108, disclose terpolymers of maleic anhydride with (i) 1-hexene, propylene, isobutylene, styrene, isoprene or 1,3-butadiene, and (ii) methyl methacrylate, methyl acrylate or acrylonitrile.

BRIEF SUMMARY OF THE INVENTION

The present invention provides polyamide fibrous substrates treated with water-soluble or water-dispersible maleic anhydride/alpha-olefin polymers so as to impart stain-resistance to the substrates, and methods for preparing the same. Commonly, prior art materials known to be useful as stain-blockers were sulfonated phenol-formaldehyde condensates (excepting those of Fitzgerald et al., *supra*). Finding a non-sulfonated material, such as the water-soluble or water-dispersible alpha-olefin/maleic anhydride polymers of this invention, to be useful for this purpose was unexpected.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to the use of water-soluble or water-dispersible maleic anhydride/alpha-olefin polymers, or mixtures of the same, as stain-resists for fibrous polyamides. A variety of linear and branched chain alpha-olefins can be used for the purposes of this invention. Particularly useful alpha-olefins are dienes containing 4 to 18 carbon atoms, such as butadiene, chloroprene, isoprene, and 2-methyl-1,5-hexadiene; 1-alkenes containing 4 to 8 carbon atoms, preferably C_4 - $_{10}$, such as isobutylene, 1-butene, 1-hexene, 1-octene, and the like, with isobutylene being most preferred. A part of the alpha-olefins can be replaced by other monomers, e.g. up to 50 wt% of alkyl(C_1 - $_4$) acrylates, alkyl(C_1 - $_4$) methacrylates, vinyl

acetate, vinyl chloride, vinylidene chloride, vinyl sulfides, N-vinyl pyrrolidone, acrylonitrile, acrylamide, as well as mixtures of the same.

A part (1-75%) of the maleic anhydride can be replaced by maleimide, N-alkyl(C₁₋₄) maleimides, N-phenyl-maleimide, fumaric acid, itaconic acid, citraconic acid, aconitic acid, crotonic acid, cinnamic acid, alkyl(C₁₋₁₈) esters of the foregoing acids, cycloalkyl(C₃₋₈) esters of the foregoing acids, sulfated castor oil, or the like.

At least 95 wt% of the maleic anhydride co- or terpolymers have a number average molecular weight of in the range between about 700 and 200,000, preferably between about 1000 and 100,000.

In accordance with the present invention, it has been unexpectedly found that water-soluble or water-dispersible interpolymers (i.e. copolymers, terpolymers, and the like) of maleic anhydride and one or more 1-alkenes having 4 to 8 carbon atoms, particularly isobutylene, 1-hexene and 1-octene, impart excellent stain-resistance to polyamide substrates (e.g. carpeting) at low pH. Copolymers of maleic anhydride with butadiene or propylene were found by the inventor to be less effective as stain-resists on such substrates than were interpolymers of maleic anhydride and 1-alkenes containing 4 to 8 carbon atoms. Surprisingly, he found also that copolymers of maleic anhydride and at least one olefin selected from ethylene and 1-alkenes having 10 to 24 carbon atoms impart no detectable stain-resistance to such substrates.

The maleic anhydride polymers useful in the present invention can be prepared according to methods well-known in the art. The maleic anhydride polymers thus obtained can be hydrolyzed to the free acid or their salts by reaction with water or alkali, or they can also be reacted with C₁₋₄ alkyl alcohol to provide polymeric alpha-olefin/maleic acid monoesters, which have stainblocking properties. Generally, the hydrolyzed maleic anhydride polymer, or the monoester polymer, should be sufficiently water-soluble that uniform application to a fibrous polyamide surface can be achieved at an appropriate acidity. However, applications using water dispersions of the polymer mixed with a suitable surfactant may be used to impart stain-resistance.

One can blend the stain-resists of the present invention with other known stain-resists, such as phenol-formaldehyde condensation products as disclosed in U.S. Patents 4,833,009 and 4,965,325; methacrylic acid polymers disclosed in U.S. Patent No. 4,937,123; or hydrolyzed polymers of maleic anhydride and one or more ethylenically unsaturated aromatic compounds described by Fitzgerald et al., supra.

The polymers suitable for the purposes of this invention contain between about 0.7 and 1.3 polymer units derived from one or more alpha-olefin monomers per polymer unit derived from maleic anhydride. The alpha-olefin content of the polymers of this invention comprise between (a) 100 and 80 mol% of at least one 1-alkene containing 4 to 8 carbon atoms or terminally unsaturated diene containing 4 to 18 carbon atoms and (b) 0 to 20 mol% of at least one 1-alkene containing 3, or 10 to 18, carbon atoms. Polymers containing about one polymer unit derived from one or more olefin monomers per polymer unit derived from maleic anhydride are most effective in imparting stain resistance to textile substrates. The molecular weight of the polymers useful in the invention does not appear to be a limitation so long as the polymers are water-soluble or water-dispersible. Thus, for example, hydrolyzed isobutylene/maleic anhydride copolymers having number average molecular weights between about 6000 and 100,000 impart good stain-resistance to polyamide substrates. Even at a pH as low as 1.5, water-soluble isobutylene/maleic anhydride copolymers having number average molecular weights between about 6000 and 100,000 remained in solution in water at 60 °C.

The polymers suitable for the purposes of this invention can be prepared by hydrolyzing the maleic anhydride/olefin polymers according to methods well-known in the art. For example, they can be hydrolyzed to the free acid or their salts by reaction with water or alkali. Generally, the maleic anhydride polymer should be sufficiently water-soluble that uniform application to a fiber surface can be achieved at an appropriate acidity. However, applications using dispersions of the polymers with suitable surfactants may be used to impart stain-resistance.

The olefin/maleic anhydride polymers of this invention can be used as such in treating polyamide textile substrates. They can be effectively applied to polyamide fibrous substrates by a wide variety of methods known to those skilled in the art, such as:

- padding,
- spraying,
- foaming in conjunction with foaming agents,
- batch exhaust in beck dyeing equipment, or
- continuous exhaust during a continuous dyeing operation.

They can be applied by such methods to dyed or undyed polyamide textile substrates. In addition, they can be applied to such substrates in the absence or presence of a polyfluoroorganic oil-, water-, and/or soil-repellent materials. In the alternative, such a polyfluoroorganic material can be applied to the textile

substrate before or after application of the polymers of this invention thereto.

The quantities of the polymers of this invention which are applied to the textile substrate are amounts effective in imparting stain-resistance to the substrate. Those amounts can be varied widely; in general, one can use between 1 and 5% by weight of them based on the weight of the textile substrate, usually 2.5% by weight or less. The polymers can be applied, as is common in the art, at pHs ranging between about 2 and 7. However, more effective exhaust deposition can be obtained at a pH as low as 1.5. When the latter low pH is used, the preferred level of application to the textile substrate is about 2.5% by weight, based on the weight of the textile substrate. In an embodiment, a pH between about 2 and 3 is used. More effective stainblocking is obtained if the polymers are applied to the textile substrate at either 20 °C followed by heat treatment at a temperature in the range between about 50 and 150 °C for about 1 to 60 minutes, or applied at temperatures in the range between about 40 and 95 °C for about 1 to 60 minutes. For example, at a pH between about 2 and 3, a temperature between about 70 and 90 °C is preferred. However, stain-blocking can be obtained when application is effected even at that of cold tap water (10-15 °C).

The polymers of this invention can also be applied in-place to polyamide carpeting which has already been installed in a dwelling place, office or other locale. They can be applied as a simple aqueous preparation or in the form of aqueous shampoo preparation, with or without one or more polyfluoroorganic oil-, water-, and/or soil-repellent materials. They may be applied at the levels described above, at temperatures described, and at a pH between about 1 and 12, preferably between about 2 and 9.

The following Examples are given to illustrate the invention not limit it. Unless otherwise indicated, all parts and percentages are by weight and temperatures in the Examples and Tests are in degrees Celsius. In the examples that follow, stain resistance was measured by the technique described below.

EXAMPLE 1

A butadiene/maleic anhydride copolymer having a number average molecular weight of about 5,000 to 10,000 and commercially available as a hydrolyzed product, "Lindron" 10 (Lindau Chemical), was diluted with water to a 10 wt% active ingredient solution. A 1 wt% aqueous solution of the copolymer at 60 °C became cloudy at a pH of about 2.0.

EXAMPLE 2

A 500 ml autoclave was charged with 40 g of maleic anhydride (0.408 mole), 300 ml of ethylbenzene and 4.3 g of 70 wt% of benzoyl peroxide. It was closed, vented twice with propylene and heated under stirring to 70 deg.C. The autoclave was then pressurized with propylene to 200 psi. After agitation for 3 hours at 70 °C, a solution of 2.7 g of 70 wt% benzoyl peroxide in 10 ml of ethylbenzene was blown into the reactor and the reaction was continued at 70 °C for another 14 hours. The vessel was then cooled and vented. The maleic anhydride/propylene copolymer product, in form of a dispersion, was discharged and filtered giving 46.7 g of a white powder having a number average molecular weight, by gel permeation chromatography (GPC), of 2150. A portion of the solid copolymer (10 g) was hydrolyzed at 80-95 °C in the presence of 82.5 g deionized water, 6.7 g 30 wt% sodium hydroxide and 2 drops of a 1% solution of benzyltriethylammonium chloride resulting after about 1 to 2 hours in a clear solution containing 10 wt% of a water-soluble maleic anhydride/propylene copolymer.

EXAMPLE 3

An isobutylene/maleic anhydride copolymer (10g) having a number average molecular weight (GPC) of 32,600 and an MW/M_n of 2.96, commercially available from Kuraray Co. (Japan) as "Isobam"-04, was hydrolyzed to a 10 wt% solution in accordance with the method described in Example 2. A 1% aqueous solution of the resulting isobutylene/maleic acid copolymer remained clear down to pH 1.5 at 60 °C.

EXAMPLE 4

An isobutylene/maleic anhydride copolymer (10g) having a number average molecular weight (GPC) of 91,400 and an MW/M_n of 2.86, commercially available from Kuraray Co. (Japan) as "Isobam"-10, was hydrolyzed to a 10 wt% solution by the method described in Example 2. A 1% aqueous solution of the resulting water-soluble maleic anhydride/isobutylene copolymer at 60 °C became cloudy at pH 1.6.

EXAMPLE 5

An isobutylene/maleic anhydride/ N-phenylmaleimide terpolymer (10g) having a molecular weight of about 40,000 (GPC), commercially available from Kuraray Co. (Japan) as BM-30 polymer, was hydrolyzed to a 10 wt% solution by the method described in Example 2. A 1% aqueous solution of the resulting water-soluble maleic anhydride/isobutylene/maleimide terpolymer at 60 °C became cloudy at pH 2.5.

EXAMPLE 6

A solution of maleic anhydride (9.8g - 0.1 mol) and 1-hexene (8.4g - 0.1 mole) in propylene glycol methyl ether acetate (30G) was heated under agitation and nitrogen to 60 deg.C. A solution of 2.5 g of 75 wt% t-butyl peroxyneodecanoate in 6 g of propylene glycol methyl ether acetate was then injected into the reaction vessel within half hour via a syringe pump. The reactants were agitated for another 2 hours at 60 °C before being cooled to room temperature. The product was then poured into methanol which caused precipitation of a white solid which was filtered and air dried to give 10.5 g of a maleic anhydride/1-hexene copolymer. Hydrolysis was carried out by a procedure similar to that described in Example 2.

EXAMPLE 7

A solution of 9.8 g of maleic anhydride (0.1 mole) and 11.2 g of 1-octene (0.1 mole) in 30 g of propylene glycol methyl ether acetate was heated under agitation and nitrogen to 95 °C. A solution of 2 g of t-butyl peroxy-2-ethylhexanoate in 6 g of propylene glycol methyl ether acetate was then injected into the reaction vessel within half hour via a syringe pump. The reactants were agitated for another 2 hours at 95 °C before being cooled to room temperature. The product was then poured into methanol which caused precipitation of a white solid which was filtered and air-dried to give 12.7 g of a maleic acid/1-octene copolymer having a number average molecular weight by vapor phase osmometry (VPO) of 2800. The approximate composition of the copolymer by ¹³C NMR:

1-octene/maleic anhydride = 0.72/1.00 Hydrolysis was carried out by a procedure similar to that of Example 2. A 1% aqueous solution of the resulting maleic acid/1-octene copolymer at 60 °C became cloudy at about pH 2.7.

EXAMPLE 8

An isobutylene/maleic anhydride copolymer (50 parts) having a number average molecular weight (GPC) of 32,000, commercially available from Kuraray Co. (Japan) as "Isobam"-04, was reacted under agitation with methanol (50 parts) at reflux temperature (about 65 °C) for 23 hours. Excess methanol was then removed at reduced pressure (20 mm Hg) at 70-90 °C to give the isobutylene/maleic acid monomethyl ester which was then dissolved at room temperature in dilute ammonium hydroxide (2.5 parts of ammonia in 356 parts of water) to give a 14.5 wt % solution.

EVALUATION METHOD

Nylon fiber was treated with 1.2 wt% or 2.4 wt% stain resist at a goods-to-liquor ratio of 1:32 at a pH of 2.0 or 2.35 for 45 minutes at 80 or 95 °C. The fiber was then washed, air-dried and exposed at room temperature to a dye solution consisting of 0.2 g of FD&C Red Dye No. 40 and 3.2 g of citric acid in 1 liter of deionized water at a goods-to-liquor ratio of 1:40. After approximately 65 hours, the dye adsorbed onto the fiber was determined at a wavelength of 498-502 nm by comparing the absorbance with that of the Control. Thus a number of 90 means 90% of the dye is adsorbed, indicating little stain resistance to the dye. The lower the number, the better is the resistance to stain. The results of the evaluation are set forth in TABLE 1.

TABLE 1

EXAMPLE	% Dye Adsorbed			
	At 80 ° C		At 95 ° C	
	pH 2.0	pH 2.35	pH 2.35	pH 2.35*
1	10	24	16	17
2		48	36	19
3	2	3	3	
4		2	1	1
5		2	3	1
6		3	30	1
7		4	2	1
8		14	22	
9		6	39	12
CONTROL**			89	89

* Fiber treated with 2.4 wt% stain resist

** No stainblocker

Claims

1. A polyamide fibrous substrate having deposited on it an amount of a composition effective to impart stain-resistance to said substrate comprising a water-soluble or water-dispersible alpha-olefin/maleic anhydride polymer or a mixture of said polymers, wherein said polymer contains between about 0.7 and 1.3 polymer units derived from one or more alpha-olefin monomers per polymer unit derived from maleic anhydride, the alpha-olefin content of said polymer comprising between (a) 100 and 80 mol percent of at least one 1-alkene containing at least 4 carbon atoms or terminally unsaturated diene containing 4 to 18 carbon atoms and (b) 0 to 20 mol percent of at least one 1-alkene containing 3 or 10 to 18 carbon atoms.
2. A substrate as claimed in claim 1 wherein said polymer is a hydrolyzed polymer.
3. A substrate as claimed in claim 1 or 2 wherein said 1-alkene contains 4 to 10 carbon atoms.
4. A substrate as claimed in any one of the preceding claims wherein said polymer contains about one polymer unit derived from maleic anhydride per polymer unit derived from one or more alpha-olefin monomers.
5. A process as claimed in any one of the preceding claims wherein at least 95% by weight of said polymers have a number average molecular weight of about 700 to 200,000.
6. A process as claimed in any one of the preceding claims wherein up to 50 weight % of said alpha-olefin is replaced by one or more of a C₁ to C₄ alkyl acrylate or methacrylate, vinyl acetate, vinyl chloride, vinylidene chloride, vinyl sulfide, N-vinyl pyrrolidone, acrylonitrile, or acrylamide, or mixtures of the same.
7. A process as claimed in any one of the preceding claims wherein up to 75 weight % of said maleic anhydride is replaced by maleimide, N-alkyl (C₁₋₁₄) maleimides, N-phenyl-maleimide, fumaric acid, itaconic acid, citraconic acid, aconitic acid, crotonic acid, cinnamic acid, alkyl (C₁₋₁₈) or cycloalkyl (C₃₋₈) esters of the foregoing acids or sulfated castor oil.
8. A process as claimed in any one of the preceding claims wherein up to 30 weight % of the maleic anhydride is replaced by acrylic or methacrylic acid.