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The title of the invention has been amended (Guidelines for Examination in the EPO, A-III, 7.3).

(54) Stain resistant polyamide textile products.

(57) Nylon or wool carpets and other polyamide products can be rendered stain resistant by impregnation with an acid-soluble addition polymer comprising sulphonic groups and aromatic, cycloaliphatic or heterocyclic groups, for instance dicyclopentadiene sulphonate, generally in combination with a hydrophilic monomer such as (meth) acrylic acid or maleic acid.

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Description

Stain Resistant Polyamide Products

Nylon fibres and other polyamide products can be dyed with acid dyes that are substantive to the dyeable dye sites of the polyamide structure, generally as a result of reaction between the acid dye and basic amino sites in the polyamide molecular structure.

When the dye is applied as a pattern it is important that it does not migrate to undyed areas and it is common to treat the dyed product with materials known as Syntans to block the undyed sites so as to prevent dyeing of these by any dye that may migrate from the dyed areas. These Syntans are sulphonated phenol formaldehyde condensation products.

A particular problem that arises with carpets and other textiles of nylon and other polyamide fibres is that they are liable to staining by accidental application of domestic stains such as fruit juice and coffee. One way of restricting such staining is by applying a water repellent coating to the fibres, but this affects detrimentally the handle of the fibres and wears off during use.

Another way is by impregnating the carpet with a material similar to the Syntans. In particular in US 4,592,940 the nylon carpet is impregnated with particular sulphonated polymeric condensation products of formaldehyde with one or more particular sulphonated phenols. Although this treatment does improve resistance to staining by acid stains, such as fruit juices, it is not entirely satisfactory. One problem is that carpets treated in this manner are more stain resistant, they are prone to yellowing when exposed to sunlight or any strong light rich in ultraviolet, and so such carpets tend to yellow during use, especially in areas exposed to sunlight. Another problem is that the treatment does not give satisfactory resistance to all types of stains that may be encountered. Thus the resistance to stains due to tea and coffee can be inadequate and, in particular, the resistance to stains due to termeric (such as mustard) is very poor.

It would be desirable to be able to provide a stain-resist treatment that gives improved stain resistance and/or less tendency to yellowing when exposed to sunlight.

A polyamide product according to the invention has undyed dyeable dye sites and substantially all the undyed dyeable dye sites are blocked by a substantially non-colouring polymer that is chemically substantive to the said undyed sites, that is soluble in aqueous acid, that can be permeated through the molecular structure of the product when the product is swollen by heat and/or moisture, and that is an addition polymer of one or more vinyl addition monomers comprising 10 to 80 mole percent monomer containing sulphonic acid groups and 10 to 80 mole percent monomer containing at least one aromatic or cycloaliphatic or heterocyclic group.

The sulphonic acid groups are essential in order that the polymer is chemically substantive to the said undyed sites. The aromatic, cycloaliphatic or heterocyclic groups are essential in order that the polymer has a relatively planar and bulky molecule in its structure since this seems necessary for good stain-resistance. Since the polymer is an addition polymer of one or more vinyl addition monomers it does not contain methylene groups condensed between phenol groups, as in U.S. 4,592,940. It appears that the presence of a methylene group between two adjacent phenyl groups provides a tendency to chromophore formation upon exposure to sunlight. By including the necessary aromatic, cycloaliphatic or heterocyclic group in the form of a vinyl addition monomer it is possible to avoid the presence of such methylene bridges. In particular, if any of the monomers used in the invention contains two rings, in particular two phenyl rings, it is preferred that these rings are not connected by a methylene bridge.

The use of the addition polymers of the invention leads to an improved combination of stain-resist properties. In particular, compared to systems such as those of U.S. 4,592,940, it gives equivalent or better stain resistance to acid stains and better stain resistance to other stains such as coffee and tea and, especially mustard, and it gives less tendency to yellowing on exposure to sunlight.

The product can be a synthetic polyamide film but is preferably a fibrous product. It can be in the form of filaments, yarn or staple fibres but is preferably in the form of a textile, most preferably a carpet. The textile has normally been dyed by one or more acid dyes either as a pale monocolour or, more usually, as a pattern.

The invention is of value during the dyeing of the textile as a replacement for conventional Syntan treatment, so as to block undyed sites and prevent staining in unwanted areas by unfixed dye.

The invention is, however, of particular value for rendering carpets and other textiles stain resistant to accidental staining.

The polyamide is generally a synthetic polyamide, i.e., a nylon, but it can be a natural polyamide, for instance wool. The product can comprise a blend of nylon and wool or it can comprise a blend of the polyamide fibres, generally nylon, and other synthetic or natural fibres.

The polymer must have a molecular size, hydrophobicity and structure such that it can be permeated into the fibres or film of polyamide in order that it can block substantially all the undyed dyeable sites, that is to say the sites that are liable to be dyed by migrating dye or accidental stain. In order to minimise the risk of the polymer being displaced from the dyeable sites by migratable dye or accidental stain it is preferred that the polymer should not easily be able to be permeated out of the molecular structure once it is substantive to the undyed sites. Preferably therefore the molecular weight and the monomers used for forming the polymer are such that the polymer can be permeated through the polyamide fibres or other polyamide product when the product is swollen by heat and/or moisture (for instance by steaming or boiling water) but is much less able to permeate through the product when the product is unswollen, e.g., in normal use. Thus the polymer can be applied while the product is swollen and will then tend to be trapped in the product when it is deswollen.

In order that the polymer can permeate into the structure its molecular weight must usually be less than 100,000, generally below 50,000 and preferably below 30,000. In order that it can be trapped in the structure after deswelling the molecular weight must usually be at least 1,000, and generally at least 5,000 and preferably at least 10,000. Best results are generally obtained when the molecular weight is in the range 10,000 to 25,000. Throughout this specification all molecular weights are weight average molecular weight Mw as measured by Gel Permeation Chromatography using polystyrene sulphonates as molecular weight standards.

The polymer must be substantially non-colouring to the polyamide product. Since some or all of this product normally includes pale areas, for instance white, the polymer should therefore be substantially colourless when applied to the polyamide product.

The polymer is made by addition polymerisation of one or more vinyl-addition monomers. These can be ethylenically unsaturated monomers or they can be monomers that behave as ethylenically unsaturated monomers. For instance a monomer may be used that includes an unsaturated ring structure which is capable of undergoing addition polymerisation with other ethylenically unsaturated monomer so that the ring is integral with the polymer backbone. Other vinyl addition monomers that may be used in the invention are ethylenically unsaturated monomers such as allyl and vinyl monomers, and the monomers generally include at least one acrylic monomer.

The polymer must contain both sulphonic groups and aromatic, cycloaliphatic or heterocyclic groups. Both types of group can be supplied by a single monomer and thus the polymer may be formed of 10 to 80 mole percent of a monomer containing a sulphonic group and an aromatic, cycloaliphatic or heterocyclic group. Comonomer that is used with this type of monomer may contain or be free of sulphonic acid groups and may contain or be free of aromatic, cycloaliphatic or heterocyclic groups. Alternatively the polymer may be formed from 10 to 80 mole percent of a linear aliphatic sulphonate and 10 to 80 mole percent of a monomer providing aromatic, cycloaliphatic or heterocyclic groups, optionally with other monomer.

The amount of sulphonic monomer is below 80 mole percent and preferably below about 50 mole percent but is normally above 10 mole percent and preferably above about 18 mole percent. Best results are generally obtained with 20 to 45 mole percent. This is based on the preferred monomers but, expressed as a weight percentage, the amount of sulphonic monomer is generally below 90 weight percent and preferably below 70 weight percent, and is generally above 15 weight percent and preferably above 30 weight percent. Best results are generally obtained when 20 to 45 mole percent, or 35 to 60 weight percent, of the monomers are sulphonic monomers.

The sulphonic monomers may be linear aliphatic monomers such as 2-acrylamido-2-methyl propane sulphonate, allyl sulphonate, vinyl sulphonate or sulpho-ethyl acrylate but preferably the sulphonic monomer includes a cyclo aliphatic or aryl moiety. Preferred sulphonic monomers are styrene sulphonate (wherein the styrene may optionally be substituted with alkyl, generally methyl, groups, and, especially, cyclo aliphatic sulphonates, most preferably cyclo pentadiene sulphonate (i.e., the monomer of formula E at column 3 line 1 of U.S. 4,547,200) wherein the cyclo aliphatic group may additionally be substituted by alkyl or aryl groups.

The copolymer should be a substantially random copolymer rather than a block copolymer, and the comonomer or comonomers must be stable to the polymerisation conditions and to the condition of use.

Particularly preferred non-sulphonated aromatic or cycloaliphatic monomers are cyclohexyl methacrylate, isobornyl methacrylate, tetrahydrofurfuryl methacrylate, N-cyclohexyl acrylamide, N-benzyl acrylamide, N-4-methyl phenyl methyl acrylamide, N-diphenyl methyl acrylamide and N,N-diphenyl methacrylamide. Aromatic, cycloaliphatic and heterocyclic monomers that are free of sulphonic acid groups are usually included in an amount of not more than 50 mole percent and usually not more than 30 weight percent. When the sulphonic monomers contains aromatic, cycloaliphatic or cycloaliphetic groups then the polymer may contain no sulphonate-free groups of this type or may contain a low amount, for instance below 30 weight percent and often below 15 weight percent. However when the sulphonic monomer does not include aromatic, cycloaliphatic or heterocyclic groups, higher amounts of sulphonate-free groups of this type may be suitable, for instance 18 to 50 mole percent or 15 to 90, usually 30 to 70, weight percent.

Preferred monomers of this general type have at least one aromatic or cycloaliphatic group. This group may be distant from the ethylenic group through which copolymerisation occurs, being connected to the group by, for instance, a polyethoxy chain. The monomer is then an associative monomer, for instance as described in EP 172025, 172723 or 216479 and the prior art discussed in those.

Preferably, however, any monomer used in the invention that includes an aromatic, cycloaliphatic or heterocyclic ring has the ring either integral with the backbone of the polymer or pendant from the backbone by a linkage of zero, 1 or 2 atoms. For instance cyclopentadiene sulphonate provides an aliphatic ring integral with the backbone, styrene provides an aromatic ring connected to the backbone through a linkage containing zero atoms, vinyl ethers would provide a linkage of 1 atom and acrylic monomers would provide a linkage of two atoms. The acrylic monomer may be an ester with, for instance, (meth) acrylic acid where the esterifying group contains a cycloaliphatic or aromatic ring, or it may be an N-monosubstituted (meth) acrylamide or N,N-disubstituted (meth) acrylamide. Suitable monomers include cyclohexyl methacrylate, isobornyl methacrylate, tetrahydrofurfuryl methacrylate, N-cyclohexyl acrylamide, N-benzyl acrylamide, N-4-methyl phenyl methyl acrylamide, N-diphenyl methyl acrylamide and N,N-diphenyl methacrylamide. Analogs of these containing at least one sulphonic acid group in the ring may also be used.

It is sometimes desirable to include also aliphatic hydrophobic monomers, especially when the cyclic monomers are all substituted by sulphonic acid groups. The amount of hydrophobic aliphatic monomer is generally from 0 to 50 weight percent, often 0 to 30 weight percent. If such a monomer is present, it is generally present in an amount of at least 5%, for instance 5 to 15 weight percent. Suitable monomers of this type include alkyl (meth) acrylates and alkyl maleates where the alkyl group contains 1 to 22 carbon atoms, and associative monomers (as discussed above) wherein the hydrophobic group is a fatty aliphatic group. Vinyl esters can be used.

It is generally preferred that the polymer is formed also from at least 10 mole percent, and usually at least 20 mole percent hydrophilic ethylenically unsaturated monomers. Thus such monomers are generally present in an amount of at least 30 to 40 weight percent and they can be present in amounts up to 80%, most usually 40 to 60 weight percent. Suitable monomers of this type include hydroxy alkyl (meth) acrylates where the alkyl generally has 1 to 4 carbon atoms and is preferably ethyl or propyl, N-vinyl formamide or acetamide, (meth) acrylamide, N-methylol- or N-alkoxy (usually n-butoxy)-acrylamide or, preferably, an ethylenically unsaturated carboxylic monomer such as (meth) acrylic acid, crotonic acid, itaconic acid, fumaric acid or, preferably, maleic or (meth) acrylic acid.

Some monomers are more able to form random copolymers than others and, for this reason, when using dicyclo pentadiene disulphonate it is particularly preferred to use maleic acid as a comonomer.

The carboxylic and sulphonic monomers may initially be supplied in the form of salts, for instance with sodium or other alkali metal.

Particularly preferred polymers for use in the invention are formed from 25 to 50 or 60 weight percent dicyclo pentadiene sulphonate, 0 to 15 or 20 weight percent dicyclo pentadiene or other hydrophobic monomer, with the balance being a randomly copolymerised monomer which is generally an carboxylic monomer, often maleic acid. Mw is preferably in the range 10 to 20,000. Other suitable monomers include monomers of substantially equal amounts of sodium styrene sulphonate and carboxylic monomer (often acrylic acid) often with from 0 to 20%, preferably 5 to 20%, styrene or other hydrophobic monomer.

The polymer may be made by conventional polymerisation techniques that are suitable for forming susbtantially random copolymers of the monomers that are being used. They may be made by free radical polymerisation, for instance using acrylamide as comonomer, but it is often preferred to make them by cationic initiation under acidic conditions, in which event the comonomer must be stable to acid and so is preferably an anionic monomer such as (meth) acrylic acid.

The polymer must be applied under pH conditions such that the sulphonate groups are substantive to dyeable sites and this generally necessitates application from acidic solution or from solution in the presence of an acid salt or an acid.

The solution of polymer is generally applied to the entire polyamide product, for instance by exhaust, pad or spray impregnation of the fibre, yarn or carpet or other textile, and permeation of the polymer into the polymeric structure of the fibres or film is generally promoted by steaming the product or by conducting the impregnation with hot aqueous solution, often boiling aqueous solution. The product may then be dried.

Although good stain resistance can be obtained using only one or more polymers of the invention, if desired these polymers can be used in conjuncticn with other stain-resist treatments, for instance of the type described in U.S. 4,592,940.

The following are examples of the invention.

Example 1

100gms of Nylon 6 cut pile white carpet of pile weight 950gm.m^{-2}, was immersed for 2 minutes in 1500mls of aqueous solution at 70° C containing 6.15gms of a 26% aqueous solutions of a 50/40/10 by weight, copolymer of sodium maleate, dicyclopentadiene sulphonate and dicyclopentadiene of molecular weight Mw = 14500, Mn = 4090 and Polydispersity 3.55, and which had been adjusted to pH 2.0 with sulphamic acid. The carpet was removed, rinsed off under cold running water, hydroextracted then dried in a fan heated oven at 60° C.

A 7cm^2 circular area of carpet pile was tested for stain resistance by pushing a 3cm diameter section of polypropylene pipe into the pile and pouring into this 10ml of a solution containing 0.08 gm l^{-1} of C.I. Food Red 17 (F.D. and C Red 40) and 0.4 gm. l^{-1} of citric acid (just enough to saturate 7 cm^2 of pile). The pipe section was removed and the wet stain left for 1 hour at 25° C then washed off in cold running water after which no red stain remained on the carpet which was assessed as 5 on the S.D.C. Grey Scale.

The yellowing propensity of the treated carpet due to light was determined by exposing the carpet to 40 hours in a Microscal Light Fastness Tester equipped with a Mercury-Tungsten Lamp. Yellowing was very slight, no worse than untreated carpet.

Example 2

100gms of Nylon 6.6 cut pile white carpet of pile weight 1290 gm.m^{-2} was padded to 100% pick up with an aqueous pad liquor of viscosity 2000 cps (Brookfield Spindle 6 @ 10 r.p.m.) comprising 94.1gms of a 17% aqueous solution of a 55/45 by weight copolymer of sodium maleate and sodium dicyclopentadiene sulphonate of molecular weight Mw = 17400, Mn = 2220 and polydispersity 7.83 and 10 gms of guar gum as viscosifier in 1000mls total adjusted to pH 7.0 with diammonium phosphate.

The padded carpet was steamed at 102° C for 10 minutes, washed in cold water and dried for 2 minutes at 130° C.

The treated carpet was tested for stain resistance and yellowing properties as in Example 1. It was found to be stain resistance (4/5 on Grey Scale) and non-yellowing properties after 40 hours in the Light Fastness Tester.

Example 3

A copolymer of 45 weight percent sodium styrene sulphonate, 45 weight percent acrylic acid and 10 weight percent styrene was formed and was impregnated into a nylon carpet as described in Example 1. Although the stain resistance was not as good as in Example 1, it was better than for the untreated carpet.

Comparative Example

100gms of Nylon 6.6 cut pile white carpet of pile weight 1290 gm m^{-2} was padded to 100% pick up with an aqueous pad liquor of viscosity 2000cps (Brookfield Spindle 6 @ 10 r.p.m.) comprising 40.0gms of a 40% aqueous solution of a 1.3:1:2.2:2.0 molar condensation product of 4,4′-dihydroxydiphenyl sulphone, phenol sulphonic acid, formaldehyde and sodium hydroxide which had been reacted under reflux for 4 hours and 10gms of guar gum as viscosifier in 1000mls total adjusted to pH 7.0 with diammonium phosphate.

The padded carpet was then steamed at 102° C for 10 minutes, washed in cold water and dried for 2 minutes at 130° C.

The treated carpet was tested for stain resistance and yellowing properties as in Example 1. It was found to have excellent stain resistance (4/5 on Grey Scale) but suffered from very severe yellowing after 40 hours in the Light Fastness Tester.

Example 4

To illustrate the benefit of adding polymers of the invention to conventional stain blocking polymers mixtures of the polymer of Example 1 were made with the polymer of the Comparative Example and compared with the latter for stain blocking against Mustard (containing Turmeric), Coffee and Kool Aid on both Nylon 6 and Nylon 66. The yellowing after 40 hours exposure to U.V. in the Light Fastness Tester was also determined. The following results were obtained.

Concn. of Polymer owo carpet		Staining			Yellowing
Example 1	Comparative Example	Coffee	Mustard	Kool Aid	
0.6	0.2	2	0.5	<0.5	4/5
0	0.8	3/4	1.5	0.5	4
0.2	0.2	2/3	0.5/1	0.5	4/5
0	0.4	4	1.5/1	1	4+

Where for staining

0.5 is good

5.0 is bad

for Yellowing

5 is good

1 is bad.

Thus the combination of a polymer of the type defined in the invention with the comparative material gave, relative to the equivalent amount of comparative material alone, less tendency to yellowing and less staining (i.e., better stain resistance) in respect of all the tested stains.

Claims

1. A polyamide product that has undyed dyable dye sites and in which substantially all the undyed dyable dye sites are blocked by a substantially non-colouring polymer that is chemically substantive to the said undyed sites, that is soluble in aqueous acid and that can be permeated through the molecular structure of the product when the product is swollen by heat and/or moisture, characterised in that the polymer is an addition polymer of one or more vinyl-addition monomers comprising 10 to 80 mole percent monomer containing sulphonic acid groups and 10 to 80 mole percent monomer containing at least one aromatic, cycloaliphatic or heterocyclic group.

2. A product according to claim 1 in which the polymer is formed from one or more vinyl addition monomers comprising 10 to 80 mole percent monomer containing sulphonic acid group and at least one aromatic, cycloaliphatic or heterocyclic ring.

3. A product according to claim 2 in which the monomers include 0 to 50 mole percent monomer that is

free of sulphonic acid group but includes at least one aromatic, cycloaliphatic or heterocyclic group.

4. A product according to any preceding claim in which the amount of monomer containing sulphonic acid groups is 18 to 50 mole percent.

5. A product according to any preceding claim in which the vinyl addition monomers include 30 to 80 weight percent hydrophilic ethylenically unsaturated monomers.

6. A product according to any preceding claim in which the polymer is formed from 25 to 60 weight percent monomer containing a sulphonic group and at least one aromatic or cycloaliphatic group, 0 to 20 weight percent other monomer containing at least one aromatic or cycloaliphatic group and 40 to 80 weight percent hydrophilic ethylenically unsaturated monomer.

7. A product according to claim 5 or claim 6 in which the hydrophilic monomer is selected from (meth) acrylic acid and maleic acid.

8. A product according to any preceding claim in which the polymer is formed from 10 to 80 mole percent dicyclopentadiene sulphonate and monomers comprising hydrophilic ethylenically unsaturated monomer.

10. A product according to claim 1 in which the polymer is a copolymer of 25 to 60 weight percent dicyclopentadiene sulphonate, 0 to 20 weight percent dicyclopentadiene and 30 to 80 weight percent maleic acid.

11. A product according to any preceding claim in which the polymer has a molecular weight of 5,000 to 50,000.

12. A product according to claim 11 in which the polymer has a molecular weight of 10,000 to 30,000.

13. A product according to any preceding claim in which the polyamide product is a carpet.

14. A product according to any preceding claim in which the polyamide product is a carpet comprising polyamide fibres.

15. A method of making a product according to any preceding claim comprising swelling the molecular structure of the polyamide by heat and/or moisture, permeating an acid solution of the said polymer into the said product while swollen and then drying the product.