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3,828,010

WATER-DISSIPATABLE POLYESTERAMIDES

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9 Claims

ABSTRACT OF THE DISCLOSURE

Water-dissipatable polyesteramides derived from monomer components which include at least one aliphatic dicarboxylic acid selected from adipic acid, pimelic acid and suberic acid, at least one diol selected from aliphatic diols containing 2 to 4 carbon atoms and polyethylene glycols, and at least one oxypropyldiamine. These polymers are useful as adhesives, coating materials, films, packaging materials and other products which can be dissolved, dispersed or otherwise dissipated in cold water, hot water or aqueous solutions.

This invention relates to sizing compositions and to fibrous articles sized therewith. In one of its more specific aspects, this invention relates to hot-melt sizing compositions for textile yarns made from linear polyesteramides.

When textile materials are to be used in the form of multifilament yarns for the fabrication of textile material, it is desirable before the weaving process to treat the warp yarn with a sizing composition (sometimes referred to as an "agent") which binds the several filaments together. This treatment strengthens the several filaments and renders them more resistant to abrasion during the subsequent weaving operations. It is especially important that the sizing composition imparts abrasion resistance to the yarns during weaving because abrasion tends to sever the yarn and to produce end breaks which lower the quality of the final woven product. It is also important that the sizing composition be one which can be subsequently removed from the yarn by scouring.

Various high-molecular weight materials have been suggested as sizing agents for yarns. Among such materials are gelatin, sodium polyacrylate, polyvinyl alcohol, and the sodium salt of a 50/50 maleic anhydride-styrene copolymer. U.S. Pat. 3,546,008 describes fibrous articles which are sized with sizing compositions comprising linear, water-dissipatable polyesters derived from at least one dicarboxylic acid component, at least one diol component, at least 20 mole percent of said diol component being a poly(ethylene glycol) and a difunctional monomer containing a $-\text{SO}_3\text{M}$ group attached to the aromatic nucleus, wherein M is hydrogen or a metal ion. These sizing materials are easily adhered to textile materials from a water-dissipation wherein the compositions thereof are dispersed or dissipated in water and the fiber is drawn through the dissipation, woven and then removed from the woven fabric with scouring. While these sizes are useful for their intended purpose, they have a serious drawback in that they must be put on the fiber from the water-dissipation. An advantage of the polyesteramides of this invention is that they may be applied to the fibers directly from the melt and are easily removed at the end of the finishing operation by dissolution in water. The prior sizes cannot be advantageously applied as a hot-melt in that their higher melt viscosities render them unsuitable for this method of application.

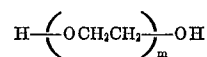
It is an object of this invention, therefore, to provide hot-melt sizing compositions and fibrous articles sized therewith. Another object of this invention is to provide sizing compositions for textile yarns, especially those yarns made from linear polyesters. Still another object

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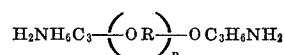
of this invention is to provide hot-melt sizing compositions which will impart abrasion resistance to textile yarns during weaving. Yet another object of this invention is to provide hot-melt sizing compositions which can be removed from textile yarns by scouring. Other objects of this invention will appear as the description of the invention proceeds.

These and other objects are obtained through the practice of this invention, one embodiment of which comprises providing a water-dissipatable polyesteramide derived from components A, B and C as follows:

- (A) at least one dicarboxylic acid selected from adipic acid, pimelic acid, suberic acid or combinations thereof, and
(B) from 20 to 50 mole percent of at least one glycol selected from aliphatic diols containing 2-4 carbon atoms and poly(ethylene glycols) having the formula



- wherein m is an integer of from 2 to about 12, and
(C) from 80 to 50 mole percent of at least one diamine, said diamine component being an oxypropyldiamine having the formula



wherein

R is ethylene, 1,2-propylene or 1,3-propylene, and n is 0 or an integer of 1 to about 12,

said mole percents of components (B) and (C) being based on the total amount of glycol and diamine in said polyesteramide, said polyesteramide having an inherent viscosity from about 0.15 to about 1.0 as measured at 25° C. at a concentration of about 0.5 gram of said polyesteramide per 100 ml. of a solvent comprised of 60 percent by weight phenol and 40 percent by weight tetrachloroethane, said polyesteramide having a ratio of alkyleneoxy linkages to dicarboxylic acid residues of from at least 1:1 to about 13:1.

Other embodiments of this invention through which the above objects are obtained comprise a process for sizing a fibrous article, said process comprising applying to said fibrous article a sizing composition as described above in the form of its hot-melt.

It has been discovered that the above-described linear water-dissipatable polyesteramides are effective as sizes when applied from a hot-melt to a variety of natural and synthetic textile yarns. Examples of such yarns include those made from polyesters such as poly(ethylene terephthalate) and poly(1,4-cyclohexylenedimethylene terephthalate), cotton, rayon, cellulose acetate, nylon, and polypropylene or blends of these fibers, etc. Therefore, although this invention will be illustrated by reference to polyester fibers, the sizing compositions of this invention may be used on these other types of textile materials.

It is necessary for greater effectiveness that a textile size be substantially scoured or removed from the woven fabric so that it will not interfere with subsequent finishing and dyeing operations. In practical terms this means that the sizing composition must be water-dissipatable. The polyesteramides of this invention contain an alkyleneoxy moiety which is hydrophilic and has a ratio of alkyleneoxy to dicarboxylic acid residues in the range from at least 1:1 to 13:1. In a preferred embodiment of this invention, the ratio of alkyleneoxy to dicarboxylic acid residue is in the range of from at least about 1:1 to about 4:1. For example, a preferred sizing composition is prepared from adipic acid, about 30 mole percent of diethylene glycol, and about 70 mole percent of ethylene bis(oxy-

propylamine), the mole percents being based on the total amount of glycol and diamine in the polyesteramide. This particular composition has a ratio of alkyleneoxy to dicarboxylic acid residues of about 1.7 and an inherent viscosity in the range of from 0.15 to about 1.0. In an especially preferred embodiment of this invention, the inherent viscosity of the polyesteramide is from 0.25 to about 0.65 and the melt temperatures of these polymers are found to be in the range of 70 to 130° C.

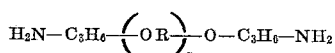
The sizes of this invention meet the requirements for an effective size, i.e., the size compositions (1) adhere the fiber bundle being sized, (2) form a sufficiently protective film so that the fiber is protected during weaving, and (3) are removable from the fiber under ordinary conditions of scouring.

The polyester yarns to be sized are the highly-polymeric fiber and film-forming, linear polyesters derived from at least one aliphatic, cycloaliphatic or aromatic dicarboxylic acid and at least one aliphatic cycloaliphatic or aromatic diol. The preparation of these polyesters and the spinning of fibers therefrom are well-known procedures and need not be detailed herein.

The aliphatic dicarboxylic acid components from which the water-dissipatable polyesteramide hot-melt sizing compositions of this invention are prepared are adipic acid, pimelic acid, and suberic acid or combinations thereof.

Examples of suitable poly(ethylene glycols) include diethylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol, hexaethylene glycol, heptaethylene glycol, octaethylene glycol, nonaethylene glycol and decaethylene glycols and mixtures thereof. Preferably, the poly(ethylene glycol) employed in the polyesteramide of the present invention is diethylene glycol or triethylene glycol or mixtures thereof. The remaining portion of the glycol component may be a 2 to 4 carbon atom aliphatic diol such as 1,3-propane diol, ethylene glycol, propylene glycol, 1,3-butanediol, 1,4-butanediol, etc.

From 80 to about 50 mole percent of at least one diamine, said diamine component being an oxypropyldiamine having the formula:



wherein R is ethylene, 1,2-propylene or 1,3-propylene and n is 0 or an integer of 1 to about 12, is useful as the diamine component of the polyesteramide of this invention. Examples of suitable diamine components of this invention are 3,3'-(diethylenetrioxo)bis(propylamine), 3,3'-(tetraethylenepentaoxo)bis(propylamine), 3,3'-(pentaethylenhexaoxo)bis(propylamine), 3,3'-(triethylenetetraoxo)bis(propylamine), etc. Generally only the diamines derived from cyanoethylated diethylene glycol and higher ethyleneoxy glycols such as tri-, tetra-, penta-ethylene glycols or higher polyethylene glycols, etc., are useful. A method of preparing these glycols is more fully illustrated in an article by N. Nazarov, G. A. Shvekhgeimer and V. A. Rudenko, Institute of Organic Chemistry of the Academy of Sciences of the U.S.S.R., June 28, 1953. It has been found that the diamines from cyanoethylated water and ethylene glycol both give water-insoluble polyesteramides with aliphatic diacids mentioned. Use of large percentages of azelaic or oxalic acids yields materials, that, although non-tacky, are water-insoluble.

Generally it is preferred that the polyesteramides of this invention be comprised of a single specific aliphatic dicarboxylic acid, a single polyethylene glycol such as diethylene glycol and a single oxypropyldiamine such as those previously described.

The polyesteramides of this invention can be prepared by well-known polymerization methods. The general procedure is to combine the dicarboxylic acid, the ether diamine and an excess of the ether glycol in the presence of an esterification catalyst. It should be understood that the term "dicarboxylic acid" includes any of the condensable derivatives of the dicarboxylic acid which could be utilized to produce a polyesteramide. Water can also be used if

desired. The reactions are heated for a period of time at about 200° C. Water is allowed to distill from the reaction during this time. The reaction is then heated for a period of time at about 250° C. at a reduced pressure to remove excess glycol and form the polymer.

The polyesteramides of this invention also have utility as hot-melt adhesives for paper, cloth, and other substrates. Because of their water-dissipatability, the polymers of this invention have many uses not open to ordinary hot-melt adhesives. For example, it is possible to apply a water-dissipation of the polymer to a substrate, allowing the water to evaporate, leaving an adherent coating of the polymer on the substrate. At some later time a bond can be formed by application of heat and pressure. Another application of this invention involves water-dissipatable films which are used for packaging detergents, dry bleach, and such products. With the use of the polyesteramides of this invention, it is possible to put package and all in a washing machine whereupon the package disintegrates readily in hot water but is relatively unaffected by moisture at ordinary room temperatures. Films of the present polyesteramides have such properties and are useful for this application.

Various additives may also be incorporated into the sizing composition to achieve specific results. Examples of such additives include titanium dioxide, dyes, other pigments and stabilizers such as antioxidants, etc.

Whenever the term "inherent viscosity" (I.V.) is used in this description, it will be understood to refer to viscosity determinations made at 25° C. using 0.5 gram of polymer per 100 ml. of a solvent composed of 60% phenol and 40% tetrachloroethane as parts by weight. In addition, whenever the terms "dissipatable," "dissipated" or "dissipate," are used in this description, it will be understood to refer to the activity of a water, aqueous or caustic aqueous solution on the polymer. The terms are specifically intended to cover those situations wherein the solution dissolves and/or disperses the polyester or polyesteramide therein and/or therethrough. Furthermore, whenever the word "water" is used in this description, it includes not only aqueous solutions but also hot aqueous solutions and caustic aqueous solutions.

The following examples are included for a better understanding of this invention.

EXAMPLE 1

This example describes a composition containing adipic acid, 73 mole percent 3,3'-(ethylenedioxy)bis(propylamine) and 27 mole percent diethylene glycol. Into a 500-ml. round bottom flask are placed 73 g. of adipic acid, 61.6 g. of 3,3'-(ethylenedioxy)bis(propylamine) and 10 ml. of water. This mixture is stirred under nitrogen while heating in a metal bath for 1.5 hours. The bath is held at 150° C. for about 10 minutes, then raised to 200° C. Water is allowed to distill. After adding 100 parts/M titanium as titanium tetraisopropoxide, the reaction is continued under the same conditions for 1 hour and 15 minutes. Heating of the reaction is stopped and 21.2 g. of diethylene glycol is added. Heating is continued under the same conditions for 1 hour and 10 minutes. The reaction is continued with stirring and heating at 200° C. while gradually applying a reduced pressure to 0.3 torr. After 1 hr. and 25 minutes under reduced pressure to remove excess glycol, the reaction is vented to nitrogen and cooled. The resulting polymer has an inherent viscosity of 0.18 and forms a solution at 20 wt. percent in water. The polymer has a melting temperature of about 110° C.

EXAMPLE 2

Using a procedure similar to Example 1, a polyesteramide containing adipic acid, 28 mole percent diethylene glycol and 72 mole percent 3,3'-(ethylenedioxy)bis(propylamine) is prepared to an inherent viscosity of 0.27.

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For preparation of this polymer, 73 g. of adipic acid, 52.8 g. of 3,3'-(ethylenedioxy)bis(propylamine), 31.8 g. of diethylene glycol, 200 parts/M titanium and 200 ml. of water are used. The polymer is soluble at 5 wt. percent in water at 24° C.

EXAMPLE 3

Using a procedure similar to Example 1, 73 g. of adipic acid, 61.6 g. of 3,3'-(ethylenedioxy)bis(propylamine), 21.7 g. of diethylene glycol, 20 ml. water and 100 mg. of dibutyltin dioxide are used to prepare a polyesteramide containing 35 mole percent diethylene glycol and 65 mole percent 3,3'-(ethylenedioxy)bis(propylamine). All of the reagents are combined at the start of the preparation. A temperature of 250° C. (metal bath temperature) is used to build up the polymer at reduced pressure. The polymer has an inherent viscosity of 0.47 and dissolves in water at 0.5 wt. percent polymer at 20° C.

EXAMPLE 4

A polyesteramide of adipic acid, 35 mole percent diethylene glycol, 65 mole percent 3,3'-(ethylenedioxy)bis(propylamine) is prepared as described in Example 2. The polymer with an inherent viscosity of 0.27 has a melt viscosity of 670 cp. at 160° C. as determined in a Brookfield viscometer.

EXAMPLE 5

This example illustrates the dissipatability and melt viscosity of several other polyesteramides using 3,3'-(ethylenedioxy)bis(propylamine). The polymers are prepared as in the examples above. Their composition and properties are given in the table below:

Acid	Glycol	Mole percent ^a glycol	I.V.	Melt viscosity, ^b cp.	Water dispersion ^c
Adipic....	Triethylene glycol.....	35	0.56	4,500	D
Do.....	Tetraethylene glycol....	30	0.44	1,500	D
Pimelic....	Diethylene glycol.....	35	0.42	2,230	D

^a The remainder is 3,3'-(ethylenedioxy)bis(propylamine).

^b Measured at 160° C.

^c D=dispersion at 0.5% by weight in water hot or cold.

EXAMPLE 6

This example illustrates the necessity of an ether-oxygen-containing diamine for water dissipatability. Two polyesteramides are prepared substantially as above from adipic acid, 35 mole percent poly(ethylene glycol) of 600 molecular weight, and 65 mole percent of a diamine. In the first case, the diamine is 3,3'-(ethylenedioxy)bis(propylamine) and the resultant polymer of 0.64 I.V. is water-dissipatable at 0.5% by weight in cold or hot water. In the second case, the diamine is hexamethylene diamine and the resultant polymer of 0.37 I.V. is not dissipatable and is only moderately swollen in hot water.

EXAMPLE 7

This example illustrates that at least one alkyleneoxy group per acid residue is required for water dissipatability of the polymer. A polyesteramide is prepared substantially as in the preceding examples from adipic acid, 3,3'-oxybis(propylamine) and ethylene glycol to contain 69 mole percent of diamine and 31 mole percent of glycol. This polymer has an I.V. of 0.50 and 0.69 alkyleneoxy groups per acid residue. The polymer is not water-dissipatable, showing only swelling in hot water. If the ethylene glycol is replaced with diethylene glycol, giving 1.0 alkyleneoxy groups per acid residue, the resultant polymer at 0.46 I.V. is water-dissipatable at 0.5 weight percent hot or cold. Alternatively, if the 3,3'-oxybis(propylamine) is replaced with 3,3'-(ethylenedioxy)bis(propylamine), giving 1.38 alkyleneoxy groups per acid residue, the resultant polymer at 0.45 I.V. is water-dissipatable at 0.5 weight percent hot or cold.

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EXAMPLE 8

This example illustrates the necessity of the ester linkages being in the range of 20 to 50% to insure water dissipatability. Two polyesteramides are prepared substantially as above from adipic acid, 3,3'-(ethylenedioxy)bis(propylamine), and diethylene glycol. In one, the glycol percentage is 15 mole percent; in the other, it is 55 mole percent. Both polymers are made to 0.46 I.V. and both are not water-dissipatable.

EXAMPLE 9

This example illustrates that use of an ether-oxygen-containing diamine based on 1,4-butanediol produces a polyesteramide that is not water-dissipatable. A polyesteramide is prepared from adipic acid, ethylene glycol, and 3,3'-(1,4-butylenedioxy)bis(propylamine) containing 35 mole percent glycol and 65 mole percent diamine. The I.V. of the product is 0.45. The polymer swells in hot water but is not dissipatable either hot or cold.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications may be effected within the spirit and scope of the invention.

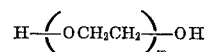
We claim:

1. A linear water-dissipatable polyesteramide derived from components A, B and C as follows:

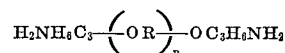
(A) at least one aliphatic dicarboxylic acid selected from

- (1) adipic acid,
- (2) pimelic acid, and
- (3) suberic acid

(B) from 20 to 50 mole percent of at least one glycol selected from aliphatic diols containing 2-4 carbon atoms and poly(ethylene glycols) having the formula



wherein m is an integer of from 2 to about 12, and (C) from 80 to 50 mole percent of at least one diamine, said diamine component being an oxypropyl-diamine having the formula



wherein

R is ethylene, 1, 2-propylene or 1,3-propylene, and n is 0 or an integer of 1 to about 12,

said mole percents of components (B) and (C) being based on a total amount of glycol and diamine in said polyesteramide, said polyesteramide having an inherent viscosity from about 0.15 to about 1.0 as measured at 25° C. at a concentration of about 0.5 gram of said polyesteramide per 100 ml. of a solvent comprised of 60 percent by weight phenol and 40 percent by weight tetrachloroethane, said polyesteramide having a ratio of alkyleneoxy linkages to dicarboxylic acid residues of from at least 1:1 to about 13:1.

2. The polyesteramide of Claim 1 wherein the ratio of alkyleneoxy linkages to dicarboxylic acid residues is from at least 1:1 to about 4:1.

3. The polyesteramide of Claim 2 wherein component (A) is adipic acid, component (B) is selected from diethylene glycol, triethylene glycol and tetraethylene glycol and component (C) is selected from 3,3'-(ethylenedioxy)bis(propylamine) and 3,3'-(diethylenetrioxo)bis(propylamine).

4. The polyesteramide of Claim 3 wherein component (C) is from 60 to about 70 mole percent of 3,3'-(ethylenedioxy)bis(propylamine).

5. The polyesteramide of Claim 4 wherein component (B) is diethylene glycol.

6. The polyesteramide of Claim 3 wherein component (C) is from 60 to 80 mole percent of 3,3'-(diethylenetrioxo)bis(propylamine).

7. The polyesteramide of Claim 6 wherein component (B) is diethylene glycol.

8. The polyesteramide of Claim 2 wherein component (A) is pimelic acid.

9. The polyesteramide of Claim 2 wherein component (A) is suberic acid.

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5 MELVIN GOLDSTEIN, Primary Examiner

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