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Johnson et al.

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[45] **Sept. 9, 1975**

[54] **SIZING ORGANIC FIBERS**

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[22] Filed: **Jan. 22, 1973**

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[52] **U.S. Cl.** **428/378;** 427/385; 427/387; 427/390; 427/394; 428/391; 428/395

[51] **Int. Cl.**[2] **D06M 15/38;** D06M 15/66

[58] **Field of Search** .... 8/115.6;117/138.8A,138.8B, 117/138.8 F, 138.8 N, 139.5 A, 139.5 CF, 161 UZ, 161 ZA, 161 UC

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Primary Examiner—P. E. Willis, Jr.
Attorney, Agent, or Firm—G. A. Skoler

[57] **ABSTRACT**

Sizing of synthetic organic fibers with an aqueous mixture of a water dispersible salt of a copolymer of ethylene and one of acrylic or methacrylic acid and a hydrolyzable organo-functional silane to provide, after said fiber is dried, improved fiber abrasion resistance, lubricity, package release, gloss, and the like.

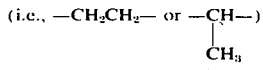
13 Claims, No Drawings

SIZING ORGANIC FIBERS

This invention relates to the sizing of synthetic organic fibers to enhance a variety of properties of the fibers. More particularly, this invention relates to the sizing of synthetic organic fibers with an aqueous mixture of a water dispersible salt of a copolymer of ethylene and one of acrylic or methacrylic acid and a hydrolyzable organo-functional silane to provide, after said fiber is dried, improved fiber abrasion resistance, lubricity, package release, gloss, and the like.

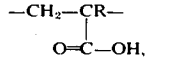
Many organic fibers are treated with organic solvent containing sizing agents for the sole purpose of enhancing the fiber's abrasion assistance. There is described herein a new sizing agent for enhancing abrasion resistance of organic fibers which is carried in water and relies upon the hydrolysis and condensation between silicon hydrolyzable groups to impart a variety of enhanced properties. In a particularly preferred embodiment of this invention, these sizing agents are most useful in the sizing of polyester fibers such as those based on polyethyleneterephthalate. The sizing agent of this invention requires less organic solvent than competitive sizing agents, yet the sizing agent of this invention wets the fiber well and can be dried quickly. Though the organo to Si ratio is below 2, preferably below about 1.5, the size of this invention provides unique lubricity, package release and higher level of gloss. The sizing agent of this invention provides a unique combination of properties to the fiber and possesses superior handling properties when used to size the fibers. The sizing agent of this invention is particularly desirable in sizing continuous filament thread, particularly continuous filament polyester thread, or spun yarn, to be used as a stitching thread in mechanical sewing operations.

The copolymers used in making the sizes of this invention are made by the copolymerization of ethylene and one or more of acrylic acid and methacrylic acid. These ethylene copolymers comprise repeating ethylene mers



(i.e., $-CH_2CH_2-$ or $-\underset{\displaystyle CH_3}{\overset{|}{C}}H-$)

and units of the formula



$$-CH_2-\underset{\displaystyle O=C-OH}{\overset{|}{C}}R-$$

where R is hydrogen or methyl. Preferably, at least 40 weight per cent of the polymer mers are ethylene and at least about 14 weight per cent of the mers contain —COOH. Most preferably, at least 50 weight per cent of the mers are ethylene and at least about 16 weight per cent of the mers contain —COOH.

The ethylene copolymers may also contain minor tercomponents, such as mers derived by adding to the copolymerization such monomers as maleic acid, fumaric acid, crotonic acid, 2-heptenoic acid, 2-ethyl-2-propenoic acid, 2-butyl-2-propenoic acid, 3-phenyl-2-propenoic acid, propylene, 1-butylene, 2-butylene, 1,3-butadiene, 2,5- or 2,6-norbornadiene, 2-norbornene, dicyclopentadiene, vinyl acetate (as well as vinyl alcohol derived therefrom), vinyl chloride, isoprene, 2-chloroprene, alkyl acrylates or methacrylates (where

the alkyl groups contain 1 to about 12 carbon atoms such as methyl, 2-ethylhexyl, dodecyl, and the like), styrene, α-methyl-styrene, betachlorostyrene, acrylamide, methacrylamide, N,N-dimethylolacrylamide, N,N-dimethylolmethacrylamide, N-vinyl-2-pyrrolidone, acrylonitrile, methacrylonitrile, alkyl vinyl ethers (such as alkyl of 1 to about 6 carbon atoms), alkyl vinyl ketones (such as alkyl of 1 to about 6 carbon atoms), and the like. However, there should be sufficient moles of ethylene and the acrylic and methacrylic carboxylic acids available to give the desired mer content thereof in the copolymer.

The ethylene copolymers typically have a molecular weight of at least about 6,000 and most preferably at least 12,000, to a molecular weight of up to 200,000 or more. The molecular weight should be sufficiently high to provide a copolymer which is solid, such as from waxy solid to tough horny resinous solid. Desirably, the copolymer has a melt index range below about 250 decigrams per minute at 190°C. (ASTM D-1238–52T). The ethylene-acrylic and/or methacrylic copolymers are desirably used as water soluble or dispersible salts when supplied to the fibers in combination with hydrolyzable organofunctional silanes.

The preferred monovalent cations forming these copolymer salts are amino groups such as



wherein each of R_1, R_2 and R_3 is either hydrogen or monovalent organic radical containing up to 10 carbon atoms. Such organic radicals may contain hydrophilic groups such as hydroxyl, amino, imino or cyclic ether groups wherein 2 of the organic radicals when taken together form a heterocyclic compound.

The monovalent organic radicals can be monovalent hydrocarbon radicals such as alkyl, cycloalkyl, aryl, alkaryl or aralkyl. Suitable alkyl radicals include methyl, ethyl and isopropyl. Representative cycloalkyl radicals include cyclobutyl, cyclopentyl and cyclohexyl. Representative aryl radicals include phenyl and naphthyl. Among the alkaryl and aralkyl radicals are, e.g., benzyl, cumyl, tolyl and xylyl radicals.

Representative monovalent organic radicals containing hydrophilic groups include hydroxyethyl (as found in monoethanolamine, diethanolamine, triethanolamine), dimethylaminopropyl, N,N-bis(hydroxyethyl) aminoethyl, N,N-bis(2-hydroxypropyl)aminoethyl, and the cation containing heterocyclic radicals as found in piperazinyl, 2,5-dimethyl piperazinyl, piperidinyl, morpholinyl, and the like.

These polymer carboxyl salts can be prepared by neutralizing the starting carboxyl containing polymer with amine bases such as trimethyl ammonium hydroxide, mono-methyltriethyl ammonium hydroxide, dimethyphenyl ammonium hydroxide and the like, aliphatic amines such as ethanolamine, diethylamine, ethylene diamine, N-(hydroxyethyl)ethylene diamine and the like, cyclic amines such as piperazine, pyridine, poperidine, morpholine and the like. Preferred bases are alkyl ammonium hydroxides, ammonium hydroxide, and dialkylamines.

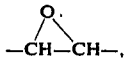
These soluble copolymers are described in U.S. Pat. Nos. 3,445,362, 3,264,272 and 3,321,819 and these

disclosures relative to such copolymers are incorporated herein by reference.

The silanes provided with the copolymer characterized by the formula:

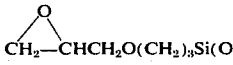
$$XR'SiY_3 \quad I$$

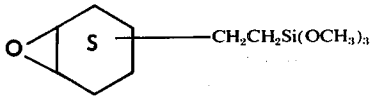
where R′ is a polyvalent saturated organic radical containing at least 3 carbon atoms in sequence therein separating X from Si, X contains a functional group which is condensible with a carboxylic acid group; e.g., functional groups such as



HN—, HS—, HO—, and the like; provided that when X is HS—, R′ may contain 2 carbon atoms in sequence therein separating X from Si; and Y is any hydrolyzable group such as alkoxy, aroxy, halogen, amino, and the like.

Specific illustrations of the aforementioned silanes are the following:



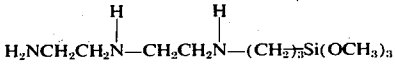


$HO(CH_2)_3Si(OCH_3)_3$

$H_2N-(-CH_2-)_3Si(OCH_2CH_3)_3$

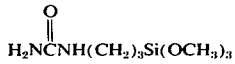
$H_2N-(-CH_2-)_3Si(OCH_3)_3$

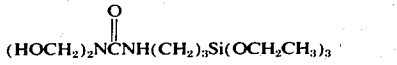
$H_2NCH_2CH_2NH(CH_2)_3Si(OCH_3)_3$

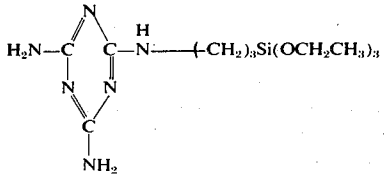


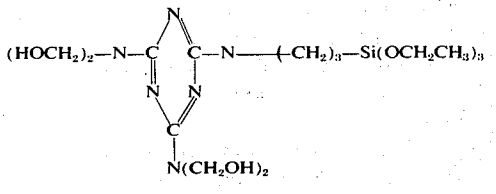
$(HOCH_2CH_2)_2N(CH_2)_3Si(OCH_2CH_3)_3$

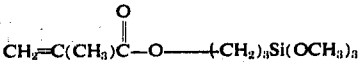
$HSCH_2CH_2CH_2Si(OCH_3)_3$

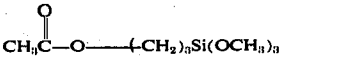


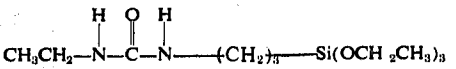


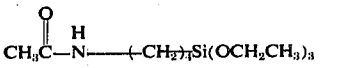


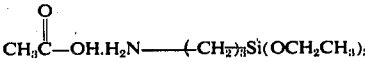


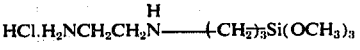












The silanes containing ester groups in the organic radical are capable of providing hydroxyl groups by in situ hydrolysis of the ester group during drying of the ethylene-acrylic acid copolymer on the substrate.

The preferred silanes in the practice of this invention contain



groups in the organo moiety, preferably -NH_2 groups. These silanes in combination with the copolymer achieve the most desirable properties, particularly in sizing polyester thread used in sewing applications.

The ethylene-acid copolymer salt is made into an aqueous dispersion, such as a solution or suspension, before the silane is added. The silane is added to the dispersion alone or admixed with water. However, a water soluble solvent which is not an active solvent for the fiber may be added to the aqueous mixture to enhance compatibility of the copolymer and/or the silane in water and also improve the ability of the aqueous copolymersilane dispersion to wet the fiber surface. In fact, in the preferred practice of this invention, alcohols such as methanol, ethanol and isopropanol are added to the dispersion for the main purpose of enhancing wettability. Generally, one attempts to keep the amount of alcohol, on a weight basis, at a level of no more than twice that of the amount of water employed.

The amount of silane employed is based on the —COO— content of the copolymer. Generally, the moles of organo functional groups of the silane do not exceed the moles of COO— present in the copolymer, and can be as low as about 0.05 mole of organofunctional groups (i.e., XR′ — in formula I above) for each mole of —COO— in the copolymer though preferably at least about 0.25 moles per —COO— group.

EXAMPLES

Sample Preparation

The polymer treating bath is prepared by diluting the ethylene/acrylic acid copolymer salt dispersion with methanol or water, and addition of the organofunctional silane. This mixture can also be prepared as a concentrate (without alcohol or water) by addition of the silane to ethylene/acrylic acid copolymer salt dispersion. This concentrate can then be diluted to the appropriate application strength when needed.

Application

A single continuous multifilament thread is passed through the treating bath containing the copolymer mixture (3–15% EAA solids), dried between 160–180°C. in the forced air heating chamber and allowed to cool before final winding. Thread speed was in the order of 10 feet/min. The cured polymer loadings were in the range of 1.5 to 9% BOWF* as calculated by difference weighing. No attempt was made to hot draw (stretch) the treated thread during this operation as is common in some commercial sizing operations.

*Based on weight fiber.

Evaluation

The ability of the cured polymer to adhere to the fiber(s) is evaluated objectively by repeatedly reversing the twist of the treated thread and at the same time rapidly flexing the thread and observing for individual filament separation and polymer flaking. Resistance to flaking was also evaluated by scraping the treated thread with the fingernail and observing the polymer removal and flaking.

For the purpose of rating the characteristics of the treated thread the following scale was established:

For Filament Separation

1. Excellent adhesion
2. Good adhesion
3. Fair adhesion
4. Poor adhesion
5. No adhesion

For resin or polymer flaking

1. No flaking
2. Slight flaking
3. Moderate flaking
4. Heavy flaking

The following working examples are illustrative of this invention. All parts referred to in the Examples are parts by weight.

EXAMPLE 1

Two hundred and twenty-one parts of ethylene/acrylic acid ammonia salt dispersion (22% solids- 22 weight per cent acrylic acid) is diluted with 279 parts methanol to which is added 8.85 parts A-1100 silane (TM of Union Carbide Corporation for $H_2NCH_2CH_2CH_2Si(OCH_2CH_3)_3$) (to provide 0.25 moles NH_2 per mole of acrylic acid). This mixture is applied, (as previously described) to 220/3 polyester sewing thread. An identical sample of thread is treated with a similar formulation without the A-1100. The treating bath polymer solids is approximately 10% by weight in all cases. Cured resin on the thread is found to be 8–9% BOWF. The treated threads are found to have the following characteristics:

	Filament Separation	Resin Flaking
with A-1100	2	3
without A-1100	4–5	3

EXAMPLE 2

One hundred and fifty parts of an ethylene/acrylic acid ammonia salt dispersion (22% solids - 22 weight per cent acrylic acid) is diluted with 332 parts methanol to which is added 5.11 parts A-1120 silane (TM of Union Carbide Corporation for $H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$), (to provide 0.25 moles NH_2 per mole acrylic acid). This mixture is applied, as previously described, to 220/3 polyester sewing thread described. The treating bath polymer solids for this sample is 6.9%. An identical sample is treated with a similar formulation but without the A-1120. Polymer solids in this treating bath is 10% by weight, in all cases. The cured resin on the sample treated with A-1120 was found to be 3.9% BOWF and the samples treated without A-1120 was 8%. The treated threads were found to have the following characteristics:

	Filament Separation	Resin Flaking
with A-1120	2–3	3
without A-1120	5	3

The above examples serve to show the effectiveness of the amino silanes A-1100 and A-1120 for improving the adhesion of ethylene/ acrylic acid copolymers. Even at lower solids concentration as shown in Example 2 the silane still shows its effectiveness relative to the similar resin system, without silane, applied at a higher concentration.

EXAMPLE 3

The formulation of Example 1 is repeated but using water as the diluent and compared with formulation of Example 1 containing A-1100 for sizing characteristics on 220/3 polyester thread. Treating bath polymer solids are 10% and resin loadings on the treated thread are approximately 8% in the case of the formulation of Example 1, and 10% in the case of the formulation of this example. The treated threads are found to have the following characteristics:

	Filament Separation	Resin Flaking
Example 1	2	3
Example 3 (using H_2O)	4	3–4

This example demonstrates advantages in using methanol as the diluent for the sizing mixture as opposed to water.

EXAMPLE 4

227.3 parts ethylene/acrylic acid ammonia salt dispersion of Example 1 is diluted with 240.4 parts methanol. After thoroughly mixing, 22.4 parts of A-1100 silane is added (0.75 moles NH_2 per mole of acrylic acid). This mixture gelled. A second preparation is made in which the dialkylamine salt of the ethylene/acrylic acid copolymer is prepared by diluting 227.3 parts ethylene/acrylic acid ammonia salt dispersion with 240.4 parts methanol and then adding 9.9 parts diethylamine (1:1 mole ratio of amine to acrylic acid). After thoroughly mixing these ingredients 22.4 parts of A-1100 silane is added (0.75 moles NH_2 per mole of acrylic acid). This mixture is stable. This mixture is applied to 220/3 polyester sewing thread as previously described. The thread size has a filament separation rating of (1) and a resin flaking rating of (1). The incorporation of an amine or use of an amine salt of stronger base strength than the A-1100 results in a stable treating solution. The organic amine can be either post

added to the ammonia salt dispersion or used to prepare the initial ethylene/acrylic acid salt.

EXAMPLE 5

227.3 Parts ethylene/acrylic acid ammonia salt dispersion of Example 1 is diluted with 240.4 parts methanol to which is added 9.9 parts diethylamine (1:1 mole ratio of amine to acrylic acid). After thoroughly mixing these ingredients 22.4 parts of A-1100 silane is added (0.75 moles NH_2 per mole of acrylic acid). This mixture is then applied to 220/3 polyester sewing thread as previously described. Treating bath solids were approximately 10% by weight ethylene/acrylic acid copolymer with a resin pickup of approximately 8%. The mixtures were compared to mixture with A-1100 of Example 1 for sizing characteristics:

	Moles NH_2 Silane/ Mole —COO—	Filament Separation	Resin Flaking
Example 1	0.25	2	3
This Example	0.75	1	1

The use of higher ratios of aminosilane to acrylic acid gives a more tightly crosslinked resin which is more resistant to abrasion.

EXAMPLE 6

Thread treated with a mixture containing 0.75 moles of amino silane per mole of acrylic acid are somewhat stiffer than is desirable. Reduction of the silane/acrylic acid ratio to 0.50 reduces this stiffness with only a slight reduction in the abrasion resistance of the cured resin. This formulation is a preferred formulation.

	Mole NH_2 Silane/ Mole —COO—	Filament Separation	Resin Flaking
This Example with amine as above	0.75	1	1
This Example - reduced silane ratio with amine as above	0.50	1	1–2

EXAMPLE 7

The mixture with amine of Example 4 is applied to 220/3 polyester filament sewing thread and to 210/3 nylon filament sewing thread. Treating bath solids are approximately 10% ethylene/acrylic acid polymer with a resin pickup of approximately 8%. Both treated samples are compared for characteristics.

	Filament Separation	Abrasion
(polyester)	1	1–2
(nylon)	1	1–2

What is claimed is:

1. The process which comprises treating polyester and nylon fibers with an aqueous mixture of a water dispersible salt of a copolymer of ethylene and one of acrylic or methacrylic acid which copolymer contains at least 14 weight percent, based on the weight of the copolymer, of polymer units therein derived from at least one of acrylic acid or methacrylic acid, at least 40 weight percent of the polymer units are ethylene, and said copolymer has a melt index below 250 decigrams per minute, and a hydrolyzable organo functional silane of the formula $XR'SiY_3$ wherein X contains a functional group which is condensible with a carboxylic acid, and R' is a saturated hydrocarbon radical containing at least three carbon atoms in sequence therein separating X from Si and bonded to both, provided that when X is HS-, R' may contain two carbon atoms in sequence separating the HS- from Si and Y is a hydrolyzable group, there being at least about 0.25 mole of XR' — provided by the silane for each mole of COO— present in the copolymer; whereby to adhere said copolymer to said fibers.

2. The process of claim **1** wherein the salt is an amine salt.

3. The process of claim **1** wherein the salt is an ammonium salt.

4. The process of claim **1** wherein the fiber is in the form of a thread.

5. The process of claim **4** wherein the thread is a sewing thread.

6. The process of claim **1** wherein the silane is an amino organofunctional silane.

7. The process of claim **2** wherein the fiber is a polyester fiber and the silane is an amino organo functional silane.

8. The process of claim **7** wherein the silane is gamma-amino propyl triethoxy-silane.

9. The process of claim **7** wherein the silane is gamma-(Beta-amino-ethyl) - aminopropyl triethoxy silane.

10. The product of the process of claim **1.**

11. The product of the process of claim **7.**

12. The product of the process of claim **8.**

13. The product of the process of claim **9.**

* * * * *