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COMPOSITION FOR COATING GLASS FIBERS

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This invention relates to a sizing or coating for glass fibers and particularly to water dispersed compositions for producing coatings on the fibers when grouped in strand or yarn form.

It is the general purpose of the present invention to provide an improved sizing or coating for glass fibers which insures ready fabrication of strands into yarn or woven fabrics, which improves the handleability of strands, yarns and slivers, and improves the adhesion between fibers having said coatings when such fibers are subsequently used as reinforcements in plastics, varnishes and the like.

It is well known in the art of production by mechanical drawing of a plurality of extremely fine long glass fibers, that the speed of attenuation and production of fibers is limited by the speeds at which the fibers can be formed into strands and satisfactorily wound on packages so that the strands can subsequently be unwound and processed on conventional textile machines. (For example, see U. S. Patent 2,234,986.) When the bundle of fibers is drawn from the molten glass flowing from the hot bushing, it is the common practice to press the bundle of fibers against a pad saturated with a binding liquid. (For example, see U. S. Patent 2,531,571.) The fibers pick up this binding liquid as they pass over the pad at high velocity. A satisfactory liquid for this purpose must be able to impart lubrication to the fibers as they are drawn over the pad and also must be of such qualities that it will lubricate the fibers against themselves to prevent breakage during the twisting and winding operations. Also this fluid should contain adhesive ingredients for binding the individual filaments from one bushing into one strand and this strand must then function as a single thread during the twisting process. If this strand is not well bound, it will tend to separate into many small strands or filaments which divide and make its removal from the original winding tubes almost impossible. This invention is also applicable to the slivers of staple-type fibers made by gaseous blast attenuation of molten glass.

A lubricating ingredient in the sizing liquid is thus needed to lubricate the fibers against abrasion from each other in the final yarn, and it should not inhibit the sticking properties of the binding ingredient of the sizing liquid.

It is an object of this invention to provide a coating or size for glass fibers which permits the production of said fibers at extremely high speeds, for example, above five thousand feet per minute, and yet enables the fibers to be gathered into a

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strand form and be packaged into a useful package. Another object of the invention is to provide a coating to bind the fibers together in strand form prior to twisting without fraying or subdividing before twisting.

It is a further object of the present invention to provide from a water medium a coating for the fibers that will bind the fibers in the sliver, bind down loose fiber ends and facilitate subsequent fabricating operations such as twisting and weaving. It is a further object to provide a strand of glass fibers wherein the individual fibers are provided with a coating which permits relative movement of fibers in the strand thereby preventing the breaking of the fibers as the strand is twisted and woven or braided. Another object of the invention is to provide from a water medium a coating substance which will readily distribute itself uniformly over the fibers at extremely high formation speeds. It is also an object of this invention to provide a coating on glass fibers which not only need not be removed but which improves the adhesion of the fibers in insulating varnishes, synthetic resins and the like, when the fibers in the form of woven glass fabrics or as reinforcing fibers are used in molded synthetic resins products.

In accordance with my invention, I have discovered that the foregoing objects may be attained if the individual fibers in the strand are provided with a coating comprising a hydrolyzed alkenyl silicone ester combined with one or more film-forming thermoplastic resins, and preferably also including a cationic lubricating agent, all as more particularly defined hereafter.

By hydrolyzed alkenyl silicone ester I mean the true water solutions prepared in accordance with the procedure disclosed in my co-pending application for patent Ser. No. 265,363, filed January 7, 1952. The process there disclosed provides for making a true water solution of an alkenyl silicone ester by vigorously stirring the ester in proportions up to thirty parts by weight to one hundred parts by weight of the water acidified to a pH of 3 to 4, until a clear homogeneous solution is obtained, this procedure requiring from thirty minutes to as long as six hours. Such water solutions of the hydrolyzed esters may be diluted with water to desired concentrations for application.

For the alkenyl silicone ester, I prefer to use vinyl triethoxy silane, although I may also use other esters, containing the vinyl group, for example, α -chloro-vinyl triethoxy silane, and β -chloro vinyl triethoxy silane.

By thermoplastic film-forming resin polymer emulsions is meant stable water emulsions which contain a dispersion of polymers, co-polymers or heteropolymers of acrylate or methacrylate, such as ethyl-acrylate, ethyl-methacrylate, methyl-methacrylate and butylmethacrylate; styrene; vinyl acetate; vinyl chloride; vinylidene chloride; butadiene; and chemically related polymers. These emulsions must be of the cationic or non-ionic types and must be stable in the pH range of 2 to 6. These emulsions may be made by physically dispersing the respective monomers in water under controlled pH conditions and then causing polymerization in the presence of suitable catalysts. The process of making the polymer resins is well known in the art, as shown, for example in an article by Mast and Fisher published at page 790 of volume 41 of *Industrial and Engineering Chemistry*; also in Houwink, "Elastomers and Polymers," volume 1, pages 58, 159, 167 to 174, published in 1950 by Elsevier Publishing Co., Inc.; also in Wakeman "The Chemistry of Commercial Plastics," pages 363 to 368, published by Reinhold Publishing Corporation, in 1947.

I may optionally include in the size for the glass fibers a lubricating agent of the cationic type which is commonly used in the textile industry to improve softness and hand of textile fabrics, namely condensation products (amides) of monobasic or dibasic fatty acids and polyethylene amines that have been solubilized with low molecular weight acids such as acetic, methacrylic, and acrylic acids.

Illustrations of the method of preparation of the sizing liquids are shown by the following examples:

Example 1.—A solution of vinyl triethoxy silane in water (prepared as above described by vigorous stirring for relatively long times in water adjusted to a pH of 3 to 4 until a clear solution was obtained) was diluted with water so that it contained five percent by weight of solid vinyl triethoxy silane and was then added in equal parts to a nonionic or cationic emulsion of polyvinyl acetate (Swift's "Glue-bond" or "Adhesive 1482") containing 10 percent by weight of solids (polyvinyl acetate), thus providing an aqueous sizing liquid containing 2.5 percent by weight of vinyl triethoxy silane and five percent by weight of polyvinyl acetate. This sizing liquid was applied to the fibers at the time of the forming of the strand in accordance with the known procedures for sizing fibers.

Example 2.—A sizing liquid was prepared by adding ten parts by weight of a 20 percent vinyl triethoxy silane solution to ten parts by weight of a 50 percent water emulsion of polyvinyl acetate, and then adding water to give an aqueous composition containing 2 percent solid vinyl triethoxy silane and 5 percent solid polyvinyl acetate. To this liquid was added 0.2 percent by weight of tetra-ethylene pentamine amide of stearic acid solubilized with methacrylic acid. The pH of the solution was adjusted to 4.5 by addition, if necessary, of formic acid. The aqueous lubricating sizing composition was applied to the glass fibers as above described, and dried to form a coating on the fibers.

Example 3.—A sizing liquid was prepared by adding 25 parts by weight of a 10 percent vinyl triethoxy silane solution to ten parts by weight of a 50 percent emulsion of polyethyl acrylate and enough water to make one hundred parts by weight. To this was added .25 percent triethyl-

enetetramine amide of palmitic acid solubilized with acrylic acid, the pH of the final liquid being adjusted to 4.5 with acrylic acid. This sizing composition was applied to the fibers as above described, and dried to form a coating on the fibers.

Example 4.—A water solution containing two parts by weight of hydrolyzed vinyl triethoxy silane and four parts by weight of polyvinyl pyridine solubilized with acrylic acid, was prepared by mixing the water solutions. This sizing liquid was then applied to the fibers as above described, and dried to yield a coating on the fibers.

The vinyl triethoxy silane present in my sizing composition is believed to react with the glass fiber surface to produce a modified glass surface capable of reacting with unsaturated or addition type polymers when the glass fibers are used as reinforcement. The thermoplastic film-forming polymer binds the fibers together into a strand and permits the glass fibers to be handled and processed. When the glass fibers so sized are used as a reinforcement for plastics, the film of thermoplastic resin dissolves and permits the vinyl group or alkenyl on the glass surface to react with the resins being reinforced.

Illustrating the advantages of using my sizing compositions on the glass fibers used as reinforcing material in the making of plastic laminates, I have made parallel fiber laminates containing treated glass fibers with an unsaturated polyester resin (Plaskon 911) catalyzed with 1 to 2 percent by weight of benzoyl peroxide, and cured at 250° F. for one-half hour. The laminates were tested according to Federal Specification LP406a in a direction perpendicular to the length of the fibers, and showed the following results:

Fiber Treatment	Flexural Strength, p. s. i.		Retention, percent of strength
	Dry	Wet	
A.....	184,000	160,000	87
B.....	167,000	140,000	84
C.....	75,000	21,000	26

The fibers used in the above laminates were previously treated as follows:

A. A size containing 125 parts by volume of a 20 percent solution in water of hydrolyzed vinyl triethoxysilane, 50 parts by volume of a 50 percent emulsion polymer of polyvinyl acetate (Swift's Glu-bond being used as emulsifier agent), and 825 parts by volume of water, was applied to the glass fibers during the glass fiber drawing and forming operation.

B. A size as specified under A, with the addition of 0.2 percent by weight of a fatty acid amide solubilized with acid (Arnold Hoffman RL-185-a) was applied to the glass fibers during drawing and forming.

C. A commercially available glass fiber size composed of polyvinyl acetate emulsion (Swift Adhesive No. 1482), a cationic softening agent (Arnold-Hoffman RL-185), and methacrylate chromic chloride complex (E. I. du Pont de Nemours and Co., Grasselli Division, "Volan").

The advantages of my sizing composition will be apparent from the above description. The application to the fibers immediately after forming of an aqueous liquid which need only be dried, has obvious advantages in operation and safety. The improvement of the glass fiber surface so that it is held strongly as reinforcement in synthetic resin plastics compositions, makes

the treated fibers particularly valuable as reinforcing fibers. The sized fibers may be readily handled on the usual textile machinery.

I claim:

1. A method for sizing glass fibers which comprises contacting glass fibers with an aqueous emulsion prepared by adding to a quantity of water, vinyl alkoxy silane, hydrolyzing the silane at an acid pH to obtain a clear homogeneous solution, forming the emulsion by adding to said solution a film forming emulsified resinous polymer formed from ethylenically unsaturated monomers, which is capable of drying in air to a continuous film, and thereafter drying the glass fibers.

2. A method as defined in claim 1 in which the emulsion also contains a glass fiber lubricating agent.

3. A method as defined in claim 1 in which the said silane is vinyl trialkoxy silane.

4. A method as defined in claim 1 in which the said silane is vinyl triethoxy silane.

5. A method as defined in claim 1 in which the said silane is alpha-chloro-vinyl triethoxy silane.

6. A method as defined in claim 1 in which the said silane is beta-chloro-vinyl triethoxy silane.

7. A composition for sizing glass fibers to improve the adhesion thereto of resinous materials comprising a dilute aqueous emulsion consisting essentially of hydrolyzed vinyl alkoxy silane prepared by hydrolysis at an acid pH and at least one film-forming emulsified resinous polymer formed from ethylenically unsaturated monomers, and which is capable of drying in air to a continuous film.

8. A composition for sizing glass fibers to improve the adhesion thereto of resinous materials comprising an aqueous emulsion consisting essentially of a hydrolyzate of vinyl alkoxy silane and a film forming emulsified resinous material selected from the group consisting of methacrylate polymers, vinyl polymers and copolymers and mixtures thereof.

9. A composition as defined in claim 7 in which the said silane is vinyl trialkoxy silane.

10. A composition as defined in claim 7 in which the said silane is vinyl triethoxy silane.

11. A composition as defined in claim 7 in which the said silane is alpha-chloro-vinyl triethoxy silane.

12. A composition as defined in claim 7 in which the said silane is beta-chloro-vinyl triethoxy silane.

13. A composition as defined in claim 7 in

which the emulsion also contains a glass fiber lubricating agent.

14. Glass fiber having on the surface thereof a composition comprising the product of drying on the said surface an aqueous emulsion of hydrolyzed vinyl alkoxy silane prepared by hydrolysis at an acid pH and at least one film-forming emulsified resinous polymer formed from ethylenically unsaturated monomers, and which is capable of drying in air to a continuous film.

15. Glass fiber having on the surface thereof a composition comprising the product of drying on the said surface an aqueous emulsion of a hydrolyzate of vinyl alkoxy silane and a film-forming emulsified resinous material selected from the group consisting of methacrylate polymers, vinyl polymers and copolymers and mixtures thereof.

16. Glass fibers as defined in claim 14 wherein the silane in said emulsion is vinyl trialkoxy silane.

17. Glass fibers as defined in claim 14 wherein the silane in said emulsion is vinyl triethoxy silane.

18. Glass fibers as defined in claim 14 wherein the silane in said emulsion is alpha-chloro-vinyl triethoxy silane.

19. Glass fibers as defined in claim 14 wherein the silane in said emulsion is beta-chloro-vinyl triethoxy silane.

20. Glass fibers as defined in claim 14 wherein the emulsion also contains a glass fiber lubricating agent.

21. In a method for sizing glass fibers, the improvement which comprises the step of contacting the glass fiber surfaces with an aqueous emulsion consisting essentially of vinyl triethoxy-silane prepared by hydrolysis at an acid pH, a film-forming resinous material selected from the group consisting of methacrylate polymers, vinyl polymers and copolymers and mixtures thereof, and a fiber lubricating agent of the cationic type selected from the group consisting of the condensation products of monobasic fatty acids with polyethylene amine and dibasic fatty acids with polyethylene amine, said condensation products being solubilized with a low molecular weight acid.

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