United States Patent

Nalley et al.

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[54] GLASS FIBER SIZE

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[58] **Field of Search**.....117/126 GB, 126 GS, 161 UF, 117/76 T; 65/3; 260/29.60 L

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[57] **ABSTRACT**

An aqueous forming size for treating a glass fiber strand, said size consisting essentially of a polypropylene emulsion, a textile lubricant and a coupling agent. The polypropylene emulsion can contain some emulsified polyethylene. The sized strands can be further coated with an aqueous rubber adhesive composition in preparation for use as reinforcement for rubber.

9 Claims, No Drawings

GLASS FIBER SIZE

Field of the Invention

The present invention relates to a glass fiber treatment. The invention particularly relates to a novel size for treating glass fibers which are to be used in various forms as a reinforcement for resinous and rubber products.

DESCRIPTION OF THE PRIOR ART

A glass fiber strand is composed of a multitude of fine glass filaments which are formed by being drawn at a high rate of speed from molten cones of glass located at the tips of small orifices in a bushing such as shown in U.S. Pat. No. 2,133,238. During formation, the filaments are coated while moving at a speed on the order of 5,000 to 20,000 feet per minute with a size which contains a binder to give the strand integrity for workability for any standard textile or reinforcement use. If the strand does not have proper integrity, fuzzing occurs during these operations and eventually the strand breaks. The size also contains a lubricant for the filaments to prevent destruction of the strand by abrasion of the individual filaments against each other or against fiber handling equipment.

It is common practice to use glass fiber strands and glass fiber cloth as a reinforcement for resins. For such use, the glass fibers are coated with a coupling agent or finish material which makes the surface of the glass fibers substantive and compatible with the particular resins with which they are to be employed. These coupling agents greatly increase the dry and wet physical strengths of the glass fiber resin laminate.

When the glass fibers are used in the form of strand, i.e., roving or chopped strand or twisted strand, for resin reinforcement, the coupling agent is usually combined with the size and applied with the size to the fibers during their formation. The size employed is usually an aqueous dispersion or emulsion of a film forming, synthetic resinous binder, and a glass fiber textile lubricant.

Roving is formed by unwinding a plurality of strands from forming packages mounted on a creel, combining the strands in parallel form and winding the strands on a tubular support in a manner such that the combined strands can be unwound and used to form woven roving or chopped strands. Twisted strand (single end on a bobbin) is made according to conventional textile twisting techniques by removing the strand from the forming package and winding it on a twister bobbin. It is therefore necessary that the strand have good integrity, freedom from "ringer" formation upon removal from the forming package and resistance to fuzzing during the steps employed to make the twisted strand or roving and fabricate them into forms suitable for use as a resin reinforcement.

It is desired that a treatment be provided for glass fiber strand which will render the strand capable of (1) being economically processed into a form suitable for reinforcing resins and elastomers (rubber) and (2) providing improved physical properties such as increased strength to glass fiber reinforced resinous and elastomeric products. More specifically, it is desired that a strand be provided with a size which permits the strand to be processed without ringer formation and fuzzing and which is compatible with resins or elastomeric adhesives so as to provide improved physical properties to the reinforced product.

An object of this invention is to provide glass fiber strand which has been treated with a size with good "wet-out" properties. It is desirable in the formation of glass fiber-resin laminates that the resin completely impregnate the strand and wet the surfaces of the fibers as quickly as possible in order to reduce the time required to make the laminates as well as to provide a laminate with maximum possible strength. It is desirable in the formation of elastomer-reinforcing glass fiber cord that the rubber adhesive completely impregnate the cord and wet the surfaces of the individual fibers in order to provide good adhesion between the cord and elastomer to be reinforced and to provide good flexural and compressive strength properties to the reinforced elastomer product. This is especially important in the manufacture of tire cord.

It is another object of this invention to provide a glass fiber strand which is treated with a size and which can be twisted, plied and woven into fabrics for use as a resin or elastomer reinforcement without requiring heat cleaning and finishing of the cloth prior to such use as required when the glass fibers have been formed with a starch containing size.

SUMMARY OF THE INVENTION

These, and other objects are accomplished by the practice of this invention which, briefly, comprises treating glass fiber strands during their formation with an aqueous size consisting essentially of about 2 to 15 percent by weight of an aqueous polyolefin emulsion selected from the group consisting of polypropylene and polypropylene-polyethylene emulsions, 0.1 to 2.0 percent by weight of a coupling agent and 0.2 to 4 percent by weight of a textile lubricant. The aqueous size has a viscosity which has been conventionally found to be suitable for glass fiber strand forming sizes to permit adequate pick-up of size by the strand to obtain strand integrity and prevent destruction of the strand by abrasion of the individual fibers against each other.

The solids content of the polyolefin emulsion is composed of about 25 to 100 percent by weight of polypropylene and 0 to 75 percent by weight of polyethylene. The polyethylene is employed to help stabilize the emulsion of the polypropylene. As greater percentages of polyethylene are employed in the emulsion, it is preferred that the softening point of the polyethylene be higher in order to obtain good adhesion in glass fiber reinforced elastomers.

The polypropylene employed in the size has an average molecular weight in the range of about 5,300 to 7,300, and a Ring and Ball softening point of 150° to 175° C., a density of 0.85 to 1 gram per cubic centimeter and a penetration hardness (100 grams/5 seconds/72° F.) in tenths of a millimeter of 0.01 maximum. The polyethylene employed in the size has an average molecular weight in the range of about 2,000 to 10,000, a Ring and Ball softening point of about 100° to 175° C., a density of 0.85 to 1 gram per cubic centimeter and a penetration hardness (100 grams/5 seconds/25° C.) in tenths of a millimeter of 0.2 to 2.5.

Some examples of polypropylene and polyethylene which are suitable for use in the invention are as follows:

1.	Polypropylene	
	Molecular weight	6,300
	Ring and Ball Softening Point	160° C.
	Density (grams per cubic centimeter)	0.9
	Penetration Hardness (100 grams/5 seconds/72° F.) tenths of a millimeter	0.0 maximum
2.	Polyethylene	
	Molecular weight	2,500
	Ring and Ball Softening Point	106° C.
	Density (grams per cubic centimeter)	0.9
	Penetration Hardness (100 grams/ 5 seconds/25° C.) tenths of millimeter	2.2
3.	Polyethylene	
	Molecular weight	6,500–8,500
	Ring and Ball Softening Point	147° C.
	Density (grams per cubic centimeter)	0.99
	Penetration Hardness (tenths of a millimeter)	<0.5

The emulsion is prepared by melting polypropylene (and polyethylene when used), adding suitable emulsifying agents with stirring and then adding water until the water in oil emulsion inverts to an oil in water emulsion. The emulsion contains about 20 to 40 percent by weight of solids (non-aqueous ingredients) based upon the weight of the emulsion. Suita emulsifying agents include Triton X–100, Igepal C0630 and Tergitol. Polyolefin emulsions which are useful in the practice of the invention are commercially available and can be used merely by mixing the polypropylene emulsion, water, lubricant and coupling agent together in a mixing tank.

Coupling agents which may be used in the aqueous size compositions in the practice of this invention include silane and siloxane materials. For example, hydrolyzable vinyl, allyl,

beta chloropropyl, phenyl, thio-alkyl, thio-alkaryl, amino-alkyl, methacrylato, epoxy and mercapto silanes, their hydrolysis products and polymers of the hydrolysis products and mixtures of any of these are suitable for such use. Some of the silanes are disclosed in U.S. Pat. Nos. 2,563,288; 2,688,006; 2,688,007; 2,723,211; 2,742,378; 2,754,237; 2,776,910; 2,799,598; 2,832,754; 2,930,809; 2,946,701; 2,952,576; 2,974,062; 3,044,982; 3,045,036; 3,169,884; 3,207,623 and 3,211,684, the disclosures of which are incorporated herein by reference.

Another class of coupling agents which has been found to be useful are the basic (hydroxy containing) metal salts of a strong mineral acid, such as, for example, a basic chromium chloride, basic chromium sulfate, etc. These compounds are ones having a trivalent metal ion selected from the group consisting of chromium, cobalt, nickel, copper and lead, at least one hydroxyl group attached to the metal, and at least one anion of a strong mineral acid attached to the metal (as well as coordinate complexes of these compounds and mixtures thereof).

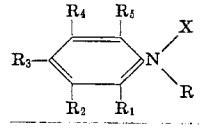
Another type of coupling agent which may be used in the practice of this invention is a complex compound of the Werner type in which a trivalent nuclear atom, such as chromium, is coordinated with an organic acid such as methacrylic acid, i.e., a methacrylic acid complex of chromic chloride. Such agents are described in U.S. Pat. No. 2,611,718. Other Werner type coupling agents having vinyl alkyl amino, epoxy, mercapto, thio-alkyl, thioalkaryl, and phenyl groups are suitable for incorporation in the size of the invention.

Mixtures of two or more of any of these coupling agents may be used.

The size may contain a textile lubricant. The lubricant is preferably cationic or non-ionic. Various conventional glass fiber textile lubricants can be used. The lubricant can be a commercially available acid solubilized, fatty acid amide. This includes both saturated and unsaturated fatty acid amides wherein the acid group contains four to 24 carbon atoms. Also included are anhydrous, acid solubilized polymers of the lower molecular weight, unsaturated fatty acid amides. A suitable material is the pelargonic acid amide of tetraethylene pentamine.

Another glass fiber lubricant which can be used in the size is an alkyl imidazoline derivative which includes compounds of the class u-alkyl N-amidoalkyl imidazolines which may be formed by causing fatty acids to react with polyalkylene polyamines under conditions which produce ring closure. The reaction of tetraethylene pentamine with stearic acid is exemplary of such reaction. These imidazolines are described more fully in U.S. Pat. No. 2,200,815. Other suitable imidazolines are described in U.S. Pat. Nos. 2,267,965, 2,268,273 and 2,355,837.

The above cationic lubricants may be used in combination with or replaced by a quaternary pyridinium compound which may be represented by the general formula:



wherein X is an anion; R is an organic group containing from one to 30 carbon atoms selected from the group consisting of alkyl, arylakyl, aryl, alkenyl and acyl; and R_1, R_2, R_3, R_4 and R_5 are each members selected from the group consisting of hydrogen, alkyl, aryl, arylalkyl, heterocyclic, halogen, alkenyl, carboxylic, alkoxy, ketonic, amido, and substituted amido. Thus, the anionic group X may be, for example, chloro, fluoro, iodo, bromo, hydroxyl, nitrate, sulfate, phosphate, etc. The group R may be, for example, methyl, ethyl, butyl, hexyl, lauryl, oleyl, benzyl, phenyl, acetyl, propionyl, benzoyl, etc. The groups R_1, R_2, R_3, R_4 and R_5 may be, for example, methyl, ethyl, propyl, cyclohexyl, furyl, pyrryl, benzyl, phenyl, chloro, bromo, iodo, fluoro, oleyl, methoxy, acetoxy, benzoxy, acetonyl, acetamido, etc. These compounds are prepared in accordance with methods common in the art by the quaternization of the corresponding pyridine bases such as, pyridine, niacin, nicotin-amide, nicotine, nicotyrine, nikethamide, 2-benzylpyridine, 3,5-dibromopyridine, 4-chloropyridine, 3-ethylpyridine, 4-methoxypyridine, 3 -phenylpyridine, 2-picoline, 3-picoline, 4-picoline, 2-picoline-4,6,dicarboxylic acid, 2,4-lutidine, 2,6-lutidine, 3,4-lutidine, 2,4-pyridine dicarboxylic acid, 4-ethyl-3-methylpyridine, 3-ethyl-4-methylpyridine, 2,4,6-trimethylpyridine, etc; with for example, an alkyl halide. In a preferred embodiment, the R group in the above formula is an aliphatic hydrocarbon radical containing from four to 18 carbon atoms.

The size may contain a wetting agent. The wetting agent is preferably cationic or non-ionic and it may also serve as an additional lubricant. Any material which is conventionally known to be useful as such and will reduce the surface tension of the size so that it is about 25 to 35 dynes per square centimeter can be used. Such materials include cetyl or stearyl monoamine hydrochloride or acetate, dodecyl amine, hexadecyl amine and secondary and tertiary derivatives of the same, for example, dodecyl methyl amine and salts thereof. Other examples of suitable wetting agents are polyoxyethylene derivatives of a sorbitol fatty acid ester such as polyoxyethylene sorbitan monostearate or polyoxyethylene sorbitan trioleate. The amount of such wetting agent employed generally ranges from about 0.01 to 1 percent by weight of the aqueous size.

The total solids (non-aqueous) content of the size is about 2 to 20 percent by weight of the size, preferably about 3 to 10 percent by weight of the size. In all events the amounts of the various ingredients should not exceed that amount which will cause the viscosity of the solution to be greater than about 100 centipoises at 20° C. Solutions having a viscosity of greater than 100 centipoises at 20° C. are very difficult to apply to glass fiber strands during their formation without breaking the strand. It is preferred that the viscosity of the size be between 1 and 20 centipoises at 20° C. for best results. The pH of the solution may generally vary from about 3 to 8.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Typical examples of the best mode of carrying out the invention are shown in the following examples of sizes:

For Resin Reinforcement

EXAMPLE I

	Ingredients	Parts by Weight (Grams)
1.	Polypropylene emulsion containing 25% by weight of polypropylene (molecular weight 6,300) and 6% by weight of emulsifying agents	5,000
2.	Polyvinyl alcohol (Elvanol 52–22 sold by DuPont)	500
3.	Imidazolamine (Emery Industries 1200–136)	200
4.	Methacryloxy propyl trimethoxy silane (A-174)	250
5.	Acetic acid	8
6.	Silicone defoamer (Sag 470)	3.8
7.	Water	Sufficient to make 10 gallons of size

ph = 9.8 % Solids = 6.3

For Elastomer Reinforcement

EXAMPLE II

Ingredients	Parts by Weight (Grams)

1. Polypropylene-polyethylene emulsion containing 12% by weight of polypropylene (molecular weight 6,300), 12% by weight of polyethylene (molecular weight 2,500) and 6% by weight of emulsifying agents (Abraze Ade sold by Proctor Chemical company)	6,000
2. Condensation product of aminoethyl ethanolamine and a hydrogenated tallow fatty acid-lubricant (SCC-137)	120
3. Stearyl amine (Alamine 7D)	40
4. Acetic acid for Alamine 7D	10
5. Versamid 140 (a polyamide resin produced by the condensation of a polycarboxylic acid with a polyamine.)	400
6. Acetic acid for Versamid 140	100
7. Gamma amino propyl triethoxy silane (A-1100)	226
8. Silicone defoamer (Sag 470)	3.8
9. Water	Sufficient to make 10 gallons of size

ph = 8.5 % Solids = 6.65 by weight

EXAMPLE III

A size as described in Example II utilizing 12 percent polyethylene having an average molecular weight of 6,500–8,500 in place of the polyethylene listed in the example.

EXAMPLE IV

A size as described in Example II utilizing 18 percent polypropylene (molecular weight 6,300) and 7 percent polyethylene (molecular weight 2,500) in the emulsion instead of the amounts of the polypropylene and polyethylene listed in the example.

The procedure for preparing the size of this invention is exemplified by the following procedure for making the size set forth in Example II. The polyolefin emulsion is poured in a size mixing tank. The SCC–137 is dissolved in hot water (140° to 150°F.) and added to the mixing tank. The Alamine 7D is dissolved in hot water with acetic acid and added to the mixing tank. The Versamid 140 is dissolved in hot water with acetic acid and added to the mixing tank. The A–1100 and SAG–470 and water are added consecutively with stirring to the mixing tank and the size is then ready for use.

The sizes are applied to the individual glass fibers during their formation in the conventional manner. The sizes are applied to the individual fibers just after their emergence from orifices in an electrically heated, platinum alloy bushing containing molten glass. The sizes are applied to the filaments prior to the time they are grouped together to form a strand by means of a roller applicator which is partially submerged in the size contained in a reservoir. Such an applicator is shown in more detail in U.S. Pat. No. 2,728,972. The fibers are grouped into a strand by a graphite guide and wound around a forming tube rotating at approximately 7,500 r.p.m. to produce a strand travel of approximately 12,000 to 15,000 feet per minute. Other methods of applying the size to the strand of glass fibers, such as pad applicator, may be employed and the strand may be formed by means other than winding on the forming tube, such as by means of a pair of rotating wheel pullers which direct the strand into a suitable collecting device.

The glass fiber strands wound on the forming tube are then dried. This may be done by heating them at a temperature and for a length of time sufficient to reduce the moisture level to that appropriate for further processing, for example, at about room temperature for 48 hours for twisting or 8 to 12 hours at 270° F. for producing roving. This drying causes the coupling agents to fix themselves to the glass surface and to produce the degree of strand integrity and moisture level required for processing the strand into roving, yarn, cord, woven cloth or woven roving. The solids content of size on the strands averages about 0.2 to 2.0 percent by weight, preferably about 0.50 percent by weight.

Glass strands sized with a size such as described in Example I are particularly useful for reinforcement of thermoplastic and thermosetting resinous products. Such reinforced products have good tensile and flexural strength. Increased physical strength, although an important and significant factor, represents only one benefit to be derived through the use of the subject sizes. Other equally beneficial and desirable aspects are the versatility and economic advantages obtained through the use of these sizes. Prior to introducing cloth woven from fiber glass strands having starch based sizes thereon into resins for reinforcement purposes, it is necessary to remove the size by literally burning it off in a heat cleaning process and subsequently apply a coupling agent to the filaments to serve as a "coupler" between the reinforcing fibers and the resin. These additional treatments involve a substantial investment in equipment and additional expense in maintenance and operation of such equipment. One substantial benefit obtained through the use of the size formulations disclosed in Example I is that one need not subject fiber glass cloth woven from yarn treated with this size to the costly heat cleaning and coupling agent treatments. One need only take the cloth woven from fiber glass yarns treated with this size, saturate it with the desired resin and shape or form said saturated cloth to whatever configuration is desired by conventional molding or laminating techniques. Thus, fabricators manufacturing resinous articles reinforced with fiber glass cloth can, through the use of cloth woven from fiber glass yarn treated with the subject sizes, produce such reinforced articles with either polyester or epoxy resins without suffering the expense of heat cleaning or coupling agent treatments.

The sized strands herein exemplified by Example II are particularly useful as a reinforcement for elastomers. In such use, a plurality of ends of strand or yarn are combined and coated with a rubber adhesive. The coated ends are twisted and then plied with other coated ends to form a coated cord. For example, five or seven ends of ECG–75S with a one-half turn twist may be combined and coated and impregnated with a rubber latex adhesive. The coated ends are heated to dry the adhesive and fix it on the combined ends of yarn. The coated ends are then twisted to impart a 2.5Z twist. The twisted ends are then plied with other twisted ends to give a balanced 2.5S plied cord. Typical cords are five-fourths for belt reinforcement and five-thirds for tire reinforcement. The cords are used as such or in a loosely woven fabric form. The fabric is used in the belt portion of bias-belt and radial ply tires.

It has been found that different adhesives must be used with different synthetic fibers to get maximum properties in different rubber stocks. A satisfactory adhesive for glass fibers and rubber is a mixture of resorcinol, formaldehyde and a terpolymer of butadiene, styrene and vinyl pyridine such as shown in U.S. Pat. No. 2,817,616. Other suitable formulations are described in U.S. Pat Nos. 2,691,614 and 2,822,311. The formulation of a suitable rubber adhesive and the coating of glass fiber strand and yarn therewith are described in the following example:

EXAMPLE V

A rubber adhesive is prepared from the following ingredients:

Ingredients	Parts By Weight
Resorcinol	352
CH_2O (37%) aqueous solution	518
NaOH	9.6
Butadiene-styrene-vinyl pyridine terpolymer latex (Gen-Tac 41% solids dispersed in H_2O)	7800
NH_4OH (28% NH_3 in H_2O)	362
H_2O	9572

These ingredients are mixed in the following manner. The Gen-Tac terpolymer latex is mixed with 1,940 parts by weight of water. Water (7,632 parts by weight) is added to a separate container. NaOH is then added and dissolved in the water in the separate container. Resorcinol is next added to the aque-

ous solution of NaOH and dissolved therein. Formaldehyde is added after the resorcinol and the mixture is stirred for 5 minutes and allowed to age at room temperature for two to six hours. The aging permits a small amount of condensation of resorcinol and formaldehyde and provides superior adhesion of the subsequently coated yarn to the rubber stock. After aging, this mixture is added to the Gen-Tac latex and the resultant mixture is stirred slowly for 15 minutes. Ammonium hydroxide is then added and the mixture is stirred slowly for 10 minutes. The ammonium hydroxide inhibits further condensation of the resorcinol formaldehyde.

Glass fiber strands sized as described in Example II are coated and impregnated with the adhesive produced as above described. Seven strands (ECG–75S) with one-half turn per inch of twist are combined in parallel relation and passed under slight tension through grooves in rotating rollers which are partially suspended in the adhesive. The pickup of adhesive is sufficient to provide a coating on the strands of about 17 to 19 percent by weight of adhesive based upon the weight of strands. 18 percent (18%) by weight of adhesive has been found to be suitable for most purposes.

Thereafter, the coated strands are passed vertically through a dielectric or microwave drying oven to remove the water and NH_3 from the adhesive. During this removal the strands appear to vibrate vigorously and further impregnation of the adhesive into the strands and onto and around the individual fibers is achieved. The coated strands next pass upwardly through a gas oven maintained at a temperature of about 350° to 500° F. to effect curing of the resorcinol formaldehyde. Further flowing and impregnating of the adhesive is accomplished during this second heating step. The curing or condensing of the resorcinol formaldehyde is free to proceed with the removal of the NH_3. The condensation is time-temperature dependent. For example, heating the coated strands for 30 seconds at 370° F. or 20 seconds at 420° F. is satisfactory. Apparatus suitable for performing the two-step heat treatment is shown in U.S. Pat No. 2,865,790.

The two-step drying and curing process provides improved uniformity and impregnation of the coating on the strands. This is evidenced by a uniformity of amount and coloring of the coating on the strands and the absence of "flags" or lumps of adhesive along the length of the coated strand as is the case with conventional coating techniques. This, in turn, provides markedly improved "flex life" of the rubber product which is reinforced with the coated strands. The two-step coating process also permits coating of the adhesive at a much faster rate than conventional coating processes which do not utilize the dielectric or microwave drying step.

Experimentation is usually necessary to determine the optimum cord construction and adhesive for the particular rubber product. In this experimentation, various screening tests are utilized to determine the properties of the reinforced rubber. The "H-Adhesion" test is one of the standard rubber industry tests.

The following rubber compounds were reinforced with glass fiber cord of ECG–75 7/0 2.5S construction and tested. The individual fibers were formed and sized as described in Example II and the strands were coated as described in Example V. The chemical identification of the ingredients in the rubber compound can be found in *Materials and Compounding Ingredients for Rubber and Plastics* published by Rubber World.

EXAMPLE VI

Ingredients	SBR - Natural Rubber Blend
SBR 1500	75
No. 1 RSS (Rubber smoked sheet)	25
HAF Black	50
ZnO	5
Stearic Acid	1
Age-Rite resin (antioxidant)	1
Sundex 790 (plasticizer)	10
Santocure (accelerative)	1
DOTG	0.2
Sulfur	2.0
H-Pull Adhesion	15.5–16.5 pounds
Strip Adhesion	
at room temperature	98–104 pounds
at 230° F. for 30 minutes	45–50 pounds
Retention (%)	43–47%
Flex Fatigue	about 610,000 cycles
Breaking strength	80–85 pounds
In-rubber tensile	97–103 pounds

Additional adhesive compositions which have been utilized in the practice of the invention are as follows:

EXAMPLE VII

An adhesive dip composition especially useful for cords which are to reinforce natural rubber and SBR stocks is as follows:

Ingredients	Parts By Weight
Butadiene-Styrene Latex (70% butadiene, 30% styrene by weight)	7800
Resorcinol	350
Formaldehyde	518
NaOH	9.6
Water	9572

This adhesive dip is prepared in the same manner as the adhesive in Example V with the exception that NH_4OH is omitted. The latex appears to act as a sufficient inhibitor to condensation of the resorcinol and formaldehyde to permit absence of NH_4OH.

EXAMPLE VIII

An adhesive dip composition especially useful for cords which are to reinforce Neoprene rubber stock is as follows:

Ingredient	% Solids	Parts by Weight
Neoprene latex (Dupont latex 460)	46%	6300
MgO	33%	315
Tergitol anionic (surfactant-Stabilizer)		63
Neozone-D (Antioxidant which prevents breakdown of Neoprene at high temperature - B-phenylnaphthyl (amine))	50%	126
ZnO	50%	315
Resorcinol		99
Formaldehyde	37%	145.8
NaOH		36
H_2O		2145.6

This adhesive is prepared in the same manner as in Example V and is aged for 24 hours at room temperature before use.

EXAMPLE IX

An adhesive dip composition especially useful for Neoprene rubber stock is as follows:

Ingredient	% Solids	Parts By Weight
Neoprene latex (Dupont latex 460)	46%	4176
Butadiene-styrene-vinyl pyridine latex	41%	1171
MgO	33%	315
NH_4OH	28%	271
Resorcinol	100%	264
Formaldehyde	37%	389
NaOH	100%	7.2
H_2O		12,570

The adhesive dip composition is prepared in the same manner as described in Example V.

The term "elastomer" as used herein and in the claims is intended to include elastic substances such as natural latex from the Hevea tree and synthetic rubber and rubber-like materials. It also includes natural and synthetic rubber and rubber-like materials which have been chemically modified such as by chlorination to improve their physical properties. Synthetic rubber includes rubber-like materials such as chloroprene, butadiene, isoprene and copolymers thereof with acrylonitrile, stryene and isobutylene. The term "elastomer" includes natural and synthetic rubber in the uncured or unvulcanized state as well as in the cured or vulcanized state.

Although the present invention has been described with respect to specific details of certain embodiments thereof, it is not intended that such details act as limitations upon the scope of the invention except insofar as set forth in the accompanying claims.

We claim:

1. In the method of forming a glass fiber strand which can be used as a reinforcement for resins and elastomers which comprises drawing glass streams through orifices in a bushing to form individual glass fibers, moving the fibers away from the bushing at a high rate of speed and forming them into a strand, applying to the fibers while they are moving at this speed an aqueous sizing solution, drying the sized glass fibers and preparing them for use as a reinforcement, the improvement whereby the sized glass fibers exhibit improved wetting by resins, which comprises sizing the glass with an aqueous size consisting essentially of 2 to 15 percent by weight of a polyolefin emulsion selected from the group consisting of polypropylene and polyethylene-polypropylene mixtures, wherein the polypropylene is present from about 25 to about 100 percent by weight of the polyolefin and the polyethylene is present from about 0 to about 75 percent by weight of the polyolefin, a coupling agent and a textile lubricant, the viscosity of the size being less than 100 centipoises at 20° C.

2. The method of claim 1 wherein the size contains 0.1 to 2 percent by weight of a coupling agent.

3. The method of claim 1 wherein the size contains 0.2 to 4 percent by weight of a glass fiber textile lubricant.

4. In the method of forming a glass fiber strand which can be used as a reinforcement for resins and elastomers which comprises drawing glass streams through orifices in a bushing to form individual glass fibers, moving the fibers away from the bushing at a high rate of speed and forming them into a strand, applying to the fibers while they are moving at this speed an aqueous sizing solution, drying the sized glass fibers and preparing them for use as a reinforcement, the improvement, whereby the sized glass fibers exhibit improved wetting by resins, which comprises sizing the glass with an aqueous size consisting essentially of 2 to 15 percent by weight of a polyolefin emulsion selected from the group consisting of polypropylene and polyethylene-polypropylene mixtures, wherein the polypropylene is present from about 25 to about 100 percent by weight of the polyolefin and the polyethylene is present from about 0 to about 75 percent by weight of the polyolefin, a coupling agent and a textile lubricant, the viscosity of the size being less than 100 centipoises at 20° C. and thereafter coating it with an aqueous elastomeric adhesive composition containing an elastomer latex and a heat curable resin, then drying the adhesive coated strand to remove the water and thereafter curing the resin by the application of additional heat.

5. The method of claim 4 wherein the size contains 0.1 to 2 percent by weight of a coupling agent.

6. The method of claim 4 wherein the size contains 0.2 to 4 percent by weight of a glass fiber textile lubricant.

7. Glass fiber strand having disposed upon the glass fibers in an amount from about 0.2 to about 2.0 percent by weight of the glass a dried residue of an aqueous size comprising, when applied, 2 to 15 percent by weight of a polyolefin emulsion selected from the group consisting of polypropylene and polyethylene-polypropylene mixtures, wherein the polypropylene is present from about 25 to about 100 percent by weight of the polyolefin and the polyethylene is present from about 0 to about 75 percent by weight of the polyolefin, a coupling agent and a textile lubricant and having disposed about said dried residue upon the glass fibers an elastomeric adhesive composition.

8. Glass fiber strand according to claim 7 wherein the size, when applied, contains 0.1 to 2 percent by weight of a coupling agent.

9. Glass fiber strand according to claim 7 wherein the size, when applied, contains 0.2 to 4 percent by weight of a glass fiber textile lubricant.

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