

[54] FIBER REINFORCED ELASTOMERS

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[58] Field of Search. 161/88, 92, 93, 143, 144, 170, 161/175, 176; 117/62.2, 76 T, 77, 79, 80, 75, 128.7, 128.4, 126 GR, 126 GQ, 126 GE, 161 A, 161 K, 161 P, 161.2 B, 161.2 LN, 161 UD, 161 ZA, 138.8 F, 138.8 N; 156/110 A, 110 C, 110 R, 308

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[57] ABSTRACT

This invention is addressed to the improvement in the bonding relationship between inorganic and organic fibers with elastomeric materials in the manufacture of fiber reinforced elastomeric products wherein impregnated bundles of fibers are provided with at least a coating of a vulcanization retarder to moderate the rate of vulcanization of the elastomeric material with which the bundles of fibers are combined to eliminate an elastomer-elastomer interface heretofore formed to thereby further improve the bonding relationship established between the fiber bundles and the elastomeric material.

36 Claims, 5 Drawing Figures

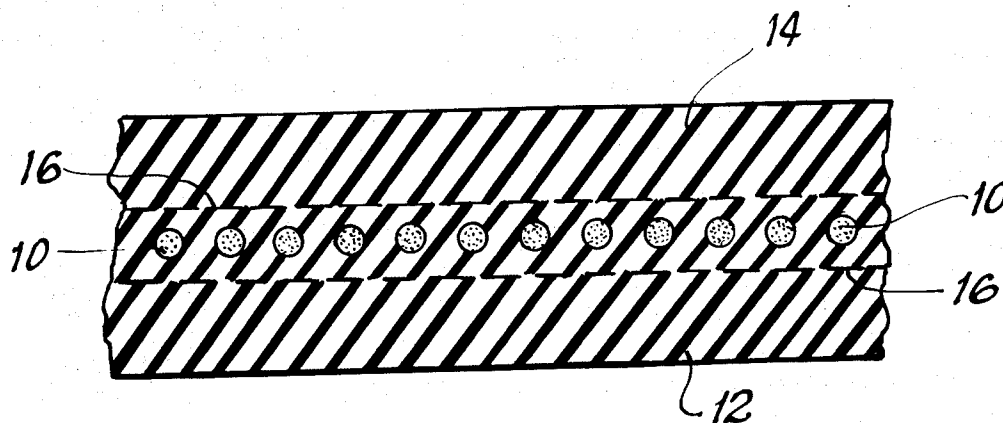


FIG. 1

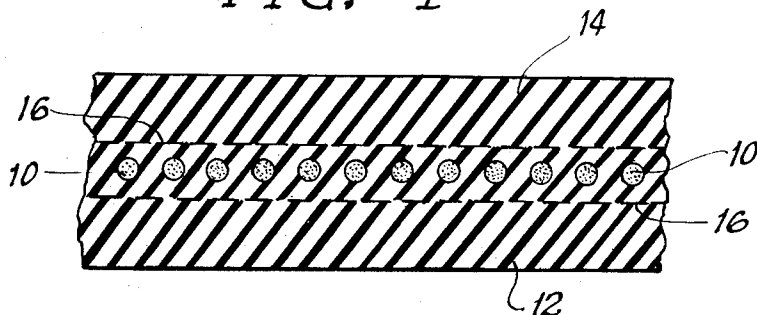


FIG. 2

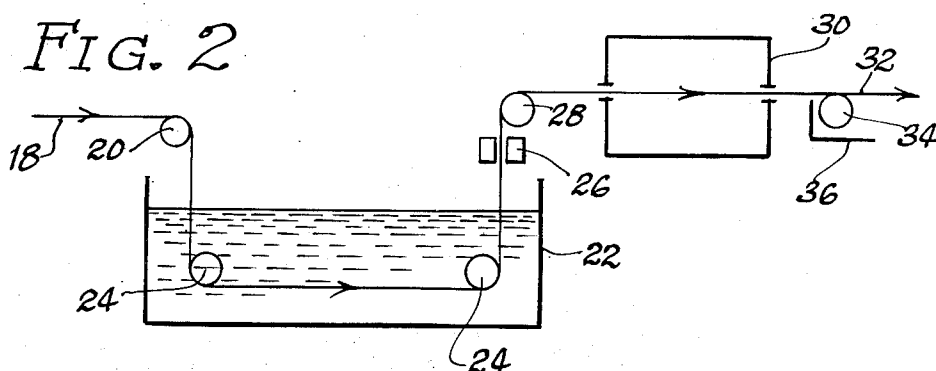


FIG. 3

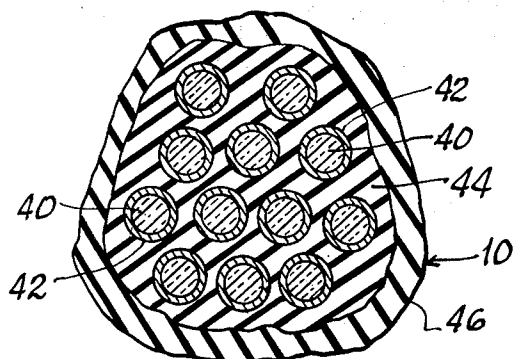


FIG. 4

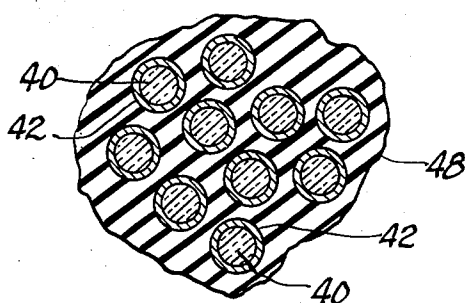
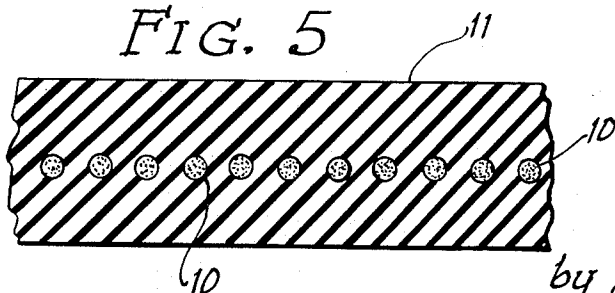


FIG. 5



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FIBER REINFORCED ELASTOMERS

This invention relates to elastomeric products reinforced or otherwise combined with organic or inorganic fibers, and more particularly to a method and composition employed in the treatment of fibers, including glass fibers, metal fibers, and organic fibers such as polyester fibers, nylon fibers and rayon fibers, to enhance the bonding relationship between the fibers and the elastomeric material for more complete utilization of the desirable characteristics of the fibers in their combination with the elastomeric materials.

As used herein, the term "elastomer" is meant to include natural rubber in the cured or uncured stage, vulcanized or unvulcanized stage, and synthetic organic elastomeric materials such as butadiene-styrene copolymer, butadiene-acrylonitrile copolymer, chloroprene, isoprene, neoprene, isobutyl rubber and the like elastomeric polymers and copolymers in their cured or uncured stages, and vulcanized or unvulcanized stages. Included also are the EPDM rubbers, such as those formed by the interpolymerization of ethylene, an alpha-monoolefin having from 3-20 carbon atoms, such as propylene, and a polyene, such as dicyclopentadiene, 1,4-hexadiene and preferably an alkylene or alkylidene norbornene, such as 5-alkylidene-2-norbornene and the like in which the alkylidene group numbers from 2-12 carbon atoms, and polysulfone rubber.

This invention is addressed to the more complete utilization of the desirable characteristics of inorganic and organic fibers as a reinforcement or as a stabilizing agent in belt manufacture, as cords, strands and fabrics to increase structure, life, wearability, and service characteristics in rubber tires, and as a reinforcement and the like in other elastomeric coated fabrics and molded elastomeric products.

It is an object of this invention to provide a new and improved method and composition for use in treating such fibers, preferably in the form of cords, yarns, strands and fabrics, hereinafter referred to as bundles, to enable more complete utilization to be made of the desirable characteristics of such fibers when used in combination with elastomeric materials in the manufacture of fiber reinforced molded products and coated fabrics.

This and other objects and advantages of the invention will hereinafter appear, and, for purposes of illustration, but not of limitation, and embodiment of the invention is shown in the accompanying drawing, in which:

FIG. 1 is a cross-sectional view of a fiber reinforced elastomeric product prepared in accordance with the prior art;

FIG. 2 is a schematic flow diagram of a method for treating impregnated fiber bundles in accordance with one concept of the present invention;

FIG. 3 is a cross-sectional view of a fiber bundle processed in accordance with the diagram shown in FIG. 2;

FIG. 4 is a cross-sectional view of a fiber bundle prepared in accordance with another concept of this invention; and,

FIG. 5 is a cross-sectional view of a fiber reinforced elastomeric product formed with a fiber bundle of the type shown in FIGS. 3 or 4 in accordance with this invention.

The combination of fibers, such as metal fibers, polyester fibers, nylon fibers, rayon fibers, and particularly glass fibers, with elastomeric material in the manufacture of fiber reinforced elastomeric products is now well known to the art. In accordance with the usual practice of forming such elastomeric products, a number of fibers are gathered together to form what is most frequently referred to as a fiber bundle, and the bundle is impregnated with an elastomer compatible material whereby the impregnant serves to completely fill the spaces between the individual fibers and form a unitary bundle structure. Thereafter, the bundles of fibers are combined in the desired manner with elastomeric materials and molded under heat and pressure to cure and/or vulcanize the elastomeric material. It is generally recognized that the function of the impregnant in the fiber bundle is to intertie the fiber surfaces to the elastomeric material in which the fiber bundles are distributed.

One of the primary problems which has been encountered in the manufacture of fiber reinforced elastomeric products is the relative inability to securely bond the fibers to the elastomeric material in which the fibers are distributed. While this problem exists with respect to polyester fibers, nylon fibers, and rayon fibers as well as other synthetic organic fibers, the problem of the bonding relationship between fibrous material and elastomeric materials is particularly severe in the case of metal fibers (e.g., wires) and glass fibers. With respect to glass fibers, it is believed that this difficulty in part stems from the completely smooth, rod-like surfaces of the glass fibers and in part from the fact that the glass fiber surfaces are highly hydrophilic in nature, thereby resulting in the formation of a thin, but tenacious film of moisture on the glass fiber surfaces almost immediately after they are formed which serves to destroy any bond, chemical or physical, which would otherwise be established between the glass fiber surfaces and the elastomeric material.

While progress has been made in promoting the bonding relationship with fibrous materials, including glass fibers, there is nevertheless room for further improvement in that it is frequently observed in the formation of fiber-reinforced elastomeric products that the fibers can literally be torn away from the elastomeric material in which they are distributed. It has been observed that when fibers are so torn away from elastomeric material in which they are distributed, the elastomeric material immediately adjacent to and in contact with the fibrous material, such as fiber bundles of the type described above, adheres to the fiber bundles. It has, therefore, been concluded that while a sufficiently secure bond between the glass fiber bundles and the elastomer immediately surrounding the bundles has been established, there is formed an interface between the elastomeric material immediately adjacent to the fiber bundles and the remainder of the elastomeric material in which the fiber bundles are distributed which represents the weakest portion of the fiber bundle-elastomer composite.

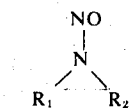
The foregoing observations can be illustrated more clearly by reference to FIG. 1 of the drawing which depicts a fiber bundle-reinforced elastomeric product prepared in accordance with the concepts of the prior art. As is shown in this figure, a plurality of fiber bundles 10 are molded between layers 12 and 14 of elastomeric material to cure and/or vulcanize the elastomeric

material to securely anchor the fiber bundles to the elastomeric material. However, the interface 16 referred to above is formed between the elastomeric material immediately adjacent to the fiber bundles 10 and the elastomeric material forming the bulk of the continuous phase 12 and 14 in which the fiber bundles are distributed.

Significant research efforts have been made in an effort to determine the nature and causes of this elastomer-elastomer interface. It is presently believed that this interface is formed as a result of unequal rates of cure and/or vulcanization throughout the elastomeric material. Thus, without limiting the present invention as to theory, it is believed that the elastomeric material 16 forming the interface between the fiber bundles 10 and the continuous phase 12 and 14 of the elastomeric material is formed as a result of overcuring of the elastomeric material immediately adjacent to the fiber bundles. It is further believed that the overcuring or overvulcanization of the elastomeric material immediately adjacent to the fiber bundles is a result of the migration of low molecular weight components from the impregnant in the fiber bundles into the elastomeric material, to thereby trigger accelerators which are conventionally blended with the elastomeric material for activation during cure and/or vulcanization, and/or to thereby serve as accelerators in their own right.

It has now been found in accordance with the present invention that the elastomer-elastomer interface referred to above can be substantially minimized or eliminated with the result that the bonding relationship between the fiber bundles is significantly improved by providing the fiber bundles with at least a thin coating of a vulcanization retarder. It has been determined that the vulcanization retarder serves to moderate the rate of vulcanization and/or cure of the elastomeric material immediately adjacent to the fiber bundles with the result that a more uniform rate of vulcanization and/or cure takes place throughout the fiber bundle-elastomer composite.

As the vulcanization retarders, use can be made of a variety of materials useful for this purpose. One preferred group of retarders are the N-nitroso amines derived from secondary amines and having a boiling point sufficiently high to minimize their elimination from the bundle during vulcanization and/or cure of the bundle-elastomer composite. Such retarders have the formula



wherein R_1 is aryl containing 6 to 14 carbon atoms, and preferably phenyl or naphthyl and R_2 is alkyl containing 2 to 20 carbon atoms (e.g., ethyl, propyl, butyl, isobutyl, pentyl, etc.), cycloalkyl containing 5 to 10 carbon atoms (e.g., cyclopentyl, cyclohexyl, etc.) or aryl containing 6 to 14 carbon atoms. In addition, R_1 and/or R_2 can be substituted by one or more substituents including amino, cyano, C_1 to C_5 alkyl, hydroxy, etc.

Representative of such retarders include N-nitrosodiphenylamine, N-nitrosoisopropylphenylamine, N-nitrosophenyl-naphthylamine, N-nitrosophenylpentylamine, N-

nitrosophenyl-ethylamine, N-nitrosotolylisopropylamine, N-nitroso-(p-aminophenyl)-phenylamine, N-nitrosophenylcyclohexylamine as well as a variety of others.

Another group of retarders which can be used in the practice of this invention are the carboxylic acids and their corresponding anhydrides or acid halides having a boiling point above 200°C to minimize elimination of the acid during cure and/or vulcanization. For example, use can be made of benzoic acid as well as substituted derivatives thereof in which the substituents are amino, cyano, C_1 to C_5 alkyl, hydroxy groups as well as a number of others. Salicylic acid has been found to be a particularly suitable retarder in accordance with the present invention.

In general, preferred acids are aromatic polycarboxylic acids containing 8–20 carbon atoms and 2–6 carboxyl groups as well as their corresponding anhydrides and acid halides.

Representative of such acids, anhydrides and acid halides are phthalic anhydride, phthalic acid, terephthalic acid, isophthalic acid, 1,3,5-benzenetricarboxylic acid, 1,2,3,4-benzenetetracarboxylic acid, 1,2,3,5-benzenetetracarboxylic acid, benzenehexacarboxylic acid, naphthalic acid, 1,2,3,4-naphthalenetetracarboxylic acid, etc.

It is also possible to use cobalt complexing agents in the practice of this invention, which have been found to serve as vulcanization retarders. Preferred cobalt complexing agents are the cobaltamines, and preferably the cobalthexammines and pentammines. Representative of such complexing agents is cobalt III hexamine chloride. However, it will be understood that a variety of other cobalt complexing agent are well known to those skilled in the art and may likewise be used in the practice of the invention. However, since many of the cobalt complexing agents are unstable in aqueous systems, it is generally desirable to avoid the use of such cobalt complexing agents in aqueous medium.

Again, without limiting the present invention as to theory, it is believed that the foregoing acidic-type vulcanization retarders are effective in providing a uniform rate of vulcanization and/or cure in a fiber reinforced elastomeric product through reaction with the low molecular weight components in the impregnant to thereby minimize or prevent migration of such components into the continuous phase formed of the elastomeric material.

One of the most preferred impregnants for use in this invention are the combinations of a basic elastomer latex and a resorcinolaldehyde resin prepared in the presence of primary and secondary alkyl amines in which the alkyl groups contain 1 to 4 carbon atoms. Such impregnants are commercially available under the trademark "Lotol" of the U.S. Rubber Co., and the method for their preparation is described in Canadian Pat. No. 435,754. As is described in this Canadian patent, resorcinol is reacted in aqueous medium with a lower aliphatic aldehyde, and preferably formaldehyde in a mole ratio of at least 2.0 moles of aldehyde per mole of resorcinol in the presence of the amine in a mole ratio of at least 1.3 moles of amine per mole of resorcinol to form an aqueous solution of the resorcinol aldehyde resin, which can be added to an alkaline elastomer latex without precipitation of the resin or coagulation of the latex.

It is believed that it is low molecular weight resorcinol-formaldehyde resin components of the combination of the amine-modified resorcinol-formaldehyde resin and elastomer latex which have a tendency to migrate into the elastomer, and the vulcanization retarders of this invention react with this low molecular weight component to minimize or prevent migration.

It is also possible to utilize, as an impregnant, terpolymer latexes in which the terpolymer is formed of butadiene, styrene and vinyl pyridine in the practice of this invention, either alone or in combination with an elastomer latex. The vinyl pyridine-butadiene-styrene terpolymer is available from the General Tire and Chemical Company under the tradename "Gentac" or from the Goodyear Tire and Rubber Company under the tradename of "Pliolite VP 100," and in which the materials are present in the weight ratio of 15 percent by weight vinyl pyridine, 15 percent by weight Styrene and 70 percent by weight butadiene.

It is believed that low molecular weight components of the terpolymer, which is alkaline in nature, react with the retarders used in this invention to prevent migration into the continuous elastomer phase to insure uniformity in vulcanization or cure.

It will be understood that the concepts of the present invention are applicable to any impregnant material containing a low molecular weight component reactive with the acidic retarders of this invention. Representative impregnants include urea-aldehyde resins, melamine-aldehyde resins, polyesters, polyamides, polyepoxides, all of which are known to the art.

The retarder may be combined with the impregnant in any convenient manner. In accordance with one embodiment of the invention, an impregnated bundle is coated with a thin coating of the retarder. However, the retarder is preferably formulated into the impregnating composition for the impregnation of a fiber bundle for best results.

The amount of the retarder employed is not critical and can be varied within wide limits. It is generally advisable that the retarder, whether present as a coating or as a component of the impregnant, constitutes from 0.1 to 25 percent by weight, and preferably 1 to 10 percent by weight of the impregnant.

As indicated above, the concepts of the present invention are applicable to a wide variety of fibers, including metal wire fibers, and fibers formed from organic materials including rayon, polyamides, polyesters, dacron and other synthetic fibers formed of resinous polymeric material. For a further description of the formation of bundles from fibers of the type described, reference is made to copending application Ser. No. 87,196, filed Nov. 5, 1970, and now abandoned the disclosure of which is incorporated herein by reference. In light of the fact that the phenomenon of the present invention stems from the prevention of migration of low molecular weight components from the impregnant system in the fiber bundle, the chemical nature of the fibers is not critical to the practice of the invention. However, the concepts of this invention have been found to be particularly suitable in the manufacture of glass fiber-reinforced elastomeric products since glass fibers have most unique properties as compared to other fibers of the type described above, and thus the preferred fibers for use in the practice of this invention are glass fibers.

Having described the basic concepts of the present invention, reference is now made to the following examples which are presented by way of illustration, and not of limitation, of the practice of the invention in treating fibrous materials to form fiber bundles embodying the concepts of this invention and the combination of such fiber bundles with elastomeric materials in the manufacture of fiber reinforced elastomeric products.

EXAMPLE 1

This example illustrates the treatment of a glass fiber bundle impregnated with a resorcinol formaldehyde latex to form a coating of a vulcanization retarder on the surface of the bundle.

Referring to FIG. 2 of the drawing, a strand 18 of glass fibers which have been preferably, although not necessarily, sized in forming is passed over a guide roller 20 for passage downwardly into an impregnating bath 22 containing the following impregnating composition:

Natural rubber latex-resorcinol formaldehyde resin (38% solids-"Lotol 5440")	25% by wt.
Water	75% by wt.

The bundle is then turned under a pair of rollers 24 to effect a sharp bend in the bundle which operates to open the bundle to facilitate more complete penetration of the aqueous impregnating composition in the bundle of sized glass fibers for complete impregnation of the bundle. The impregnated bundle is then raised from the bath for passage through a roller or die 26 which operates to remove excess impregnating composition from the bundle and to work the impregnating composition into the bundle. Thereafter, the endless bundle is advanced over roller 28 into a drying oven 30, preferably in the form of an air drying oven maintained at a temperature above ambient temperature, and preferably within the range of 150°-250° F. to accelerate removal of the aqueous diluent and to set the impregnant in situ in the fiber bundle. Drying will occur in relatively short time, generally ranging from 1-30 minutes depending somewhat on the temperature of drying.

After passage through the drying oven 30, the impregnated bundle 32 is coated with a solution of one of the retarders of this invention dissolved in an inert solvent. Application of a coating may be made by passing the impregnated bundle 32 over a roller 34 which is constantly wet with the retarder solution from bath 36. In this example, use is made of a solution of N-nitrosodiphenylamine dissolved in acetone although it will be understood that any of a variety of suitable inert solvents can be used.

The resulting bundle is shown in cross-section in FIG. 3 of the drawing. As can be seen from this figure, bundle 10 is formed of a plurality of individual glass fibers 40 having optional size coating 42 on the surfaces thereof. The impregnant 44 which completely penetrates the bundle serves to separate the glass fibers each from the other and to form a unitary bundle structure. The N-nitrosodiphenylamine forms a thin coating 46 on the dried and impregnated bundle and is thus available to moderate the cure and/or vulcanization when the bundle is combined with elastomeric materials in the manufacture of glass fiber-reinforced elastomeric products.

EXAMPLE 2

The procedure of Example 1 is repeated using a plurality of steel fibers which have been previously coated with zinc to reduce corrosion. Introduction of the impregnant composition is made in an amount to impregnate with dry solids of 10-25 percent by weight of the fiber system, and preferably 10-15 percent by weight. In formulating such impregnant compositions, it is generally desirable that an elastomer compatible material, such as the RFL employed in this example, be present in the impregnant composition in an amount sufficient to provide a composition having a solids content within the range of 10-50 percent by weight.

EXAMPLE 3

The procedure of Example 1 is again repeated using as the fibrous material, polyester fibers. Again, the impregnant composition is applied to the bundle in an amount to provide dry solids constituting from 10-25 percent by weight of the fiber system.

EXAMPLE 4

The procedure of Example 1 is again repeated using a plurality of sized glass fibers and the following impregnant composition:

Vinyl pyridine-butadiene-styrene terpolymer (41% solids — "Gentac")	30%
Water	70%

After drying, the impregnated bundle is then coated in the manner described in Example 1 with a solution of phthalic anhydride in an inert solvent (ethanol). The concentration of phthalic anhydride in solution is adjusted to provide a coating on the impregnated bundle constituting about 6 percent by weight of the system.

EXAMPLE 5

In this example, the procedure of Example 1 is again repeated using a resorcinol formaldehyde latex impregnant composition. After drying of the impregnated bundle, the bundle is coated in the manner described in Example 1 with a solution of cobalt III hexamine chloride in hexane. The bundle, after coating with the cobalt complexing agent, is found to contain about 2.7 percent by weight of the cobalt complexing agent.

EXAMPLE 6

This example illustrates the use of a vulcanization retarder in accordance with the present invention which has been formulated in the impregnant composition.

A resorcinol formaldehyde latex of the type described above is formulated with an N-nitrosodiphenylamine vulcanization retarder in accordance with the following example:

Natural rubber latex-resorcinol formaldehyde resin (38% solids—"Lotol 5440")	25%
N-nitrosodiphenylamine	3%
Water	72%

The foregoing impregnant composition containing the vulcanization retarder is then applied to a bundle of sized glass fibers in accordance with the method described in FIG. 2 of the drawing, except that the subse-

quent step of coating the treated bundle with the vulcanization retarder can be, if desired, omitted. The resulting bundle is illustrated in FIG. 4 of the drawing in which the impregnant 48 in the glass fiber bundle contains the N-nitrosodiphenylamine vulcanization retarder dispersed uniformly throughout.

Additional examples of impregnant compositions formulated to contain the vulcanization retarder in accordance with the practice of the invention may be illustrated by the following examples.

EXAMPLE 7

15	Natural rubber latex-resorcinol formaldehyde resin (38% solids—"Lotol 5440")	25%
	N-nitrosotolylisopropylamine	4%
	Water	71%

20 The foregoing composition is applied to nylon fibers in accordance with the procedure described in Example 6.

EXAMPLE 8

	Natural rubber latex-resorcinol formaldehyde resin (38% solids—"Lotol 5440")	25%
	Salicylic acid	5%
30	Water	70%

35 The foregoing impregnant composition is applied to unsized glass fibers in accordance with the method illustrated in FIG. 2 of the drawing and the procedure described in Example 6.

EXAMPLE 9

40	Vinyl pyridine-butadiene styrene terpolymer (41% solids — "Gentac")	28%
2.8%	N-nitrosophenylcyclohexylamine	
69.2%	Water	

45 The foregoing composition is applied to steel fibers having a zinc coating of their surfaces in accordance with the procedure described in Example 6.

EXAMPLE 10

50	Vinyl pyridine-butadiene styrene terpolymer (41% solids — "Gentac")	30.0%
55	Terephthalic acid	5.8%
	Water	64.2%

The foregoing impregnant composition can be used in the treatment of fibers of the type described above in accordance with the method described in Example 6.

EXAMPLE 11

60	Melamine formaldehyde resin (63% solids)	30%
	N-nitrosophenyl-naphthylamine	4%
	Water	66%

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EXAMPLE 12

Urea formaldehyde resin (average m.w. 900)	31%
1,3,5-Benzenetricarboxylic acid	6%
Water	63%

EXAMPLE 13

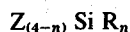
The impregnant used in this example is a polyepoxide formed of the condensation reaction product of bisphenol A and epichlorohydrin (Epon 728) marketed by Dow Chemical.

Polyepoxide	33%
N-nitrosophenylisobutylamine	5%
Water	62%

The impregnant compositions of Examples 11-13 can be used with any of the fiber systems described above.

In accordance with another embodiment of the invention, it is frequently desirable to include in the impregnating composition an anchoring agent in the form of an organo silicon compound which serves to more securely anchor the fibers, and particularly glass fibers, to elastomeric materials when bundles of impregnated fibers are combined with elastomeric materials in the manufacture of fiber reinforced elastomeric products. One of the difficulties heretofore experienced with the use of such anchoring agents is that, again, without limiting the invention as to theory, it is believed that the organo silicon anchoring agents also migrate into the rubber from the impregnant of the bundle thereby contributing to the elastomer-elastomer interface described above. However, the concepts of the present invention substantially minimize the problem of migration of these anchoring agents since the organo silicon compounds are reactive with the vulcanization retarders when the retarders are activated by heat during cure and/or vulcanization of an impregnated bundle in which the impregnant includes an anchoring agent to thereby prevent or minimize migration of the organo silicon compounds into the elastomeric continuous phase of the fiber reinforced elastomeric product.

Representative of suitable anchoring agents which can be used in the practice of this invention are the organo silicons, their hydrolysis products and polymerization products (polysiloxane) of an organo silane having the formula:



wherein Z is a readily hydrolyzable group such as alkoxyl having 1-4 carbon atoms (e.g., methoxy, ethoxy, propoxy, etc.) or halogen, such as chlorine, n is an integer from 1 to 3, and R is hydrogen or an organic group in which at least one R group is an alkyl group having 1-10 carbon atoms, such as methyl, ethyl, propyl, etc.; alkenyl having 1-10 carbon atoms, such as vinyl, allyl, etc.; cycloalkyl having 4-8 carbon atoms, such as cyclopentyl, cyclohexyl, etc.; aryl having 6-10 carbon atoms, such as phenyl, naphthyl, benzyl, etc.; alkoxy alkyl, such as methyloxyethyl, etc.; alkenylcarbonyloxyalkyl, such as carbonylpropylmethoxy, etc.; as well as the amino, epoxy, mercapto and halogen derivatives of the foregoing groups.

Illustrative of suitable silanes are ethyltrichlorosilane, propyltrimethoxy silane, vinyl trichlorosilane, allyl triethoxy silane, cyclohexylethyltrimethoxy silane, phenyl

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trichloro silane, phenyl dimethoxy silane, methacryloxypropyltrimethoxy silane, gamma-aminopropyltriethoxy silane, beta-aminovinyl diethoxy silane, N-(gamma-triethoxysilylpropyl)propylamine, gamma-aminoallyltriethoxy silane, para-aminophenyltriethoxy silane, N-(beta-aminoethyl)-gamma-aminopropyltrimethoxy silane, gamma-chloropropyltrichloro silane, glycidoxy propyltrimethoxy silane, 3,4-epoxycyclohexylethyltrimethoxy silane, gamma-mercaptopropyltrimethoxy silane as well as a wide variety of others. It will be understood that the foregoing may be used in the form of the silane, the silanol or the polysiloxane formed by one or more of the foregoing materials.

The organo silanes are generally present in the impregnant composition in an amount within the range of 0.1 to 5 percent by weight.

Examples of impregnant compositions formulated to include such silanes may be illustrated by the following examples.

EXAMPLE 14

Natural rubber latex-resorcinol formaldehyde resin (38% solids-"Lotol 5440")	25%
Gamma-aminopropyltriethoxy silane	1%
N-nitrosodiphenylamine	6%
Water	68%

EXAMPLE 15

Vinyl pyridine-butadiene-styrene terpolymer (41% solids-"Gentac")	30%
3,4-epoxycyclohexylethyl-trimethoxy silane	1.5%
Phthalic anhydride	6.0%
Tetramethyl ammonium hydroxide	4.0%
Water	58.5%

EXAMPLE 16

Melamine formaldehyde resin (63% solids)	31.0%
Delta-aminobutyltriethoxy silane	1.2%
N-nitrosophenylcyclohexylamine	4.0%
Water	63.8%

When formulating an anchoring agent into the impregnant compositions in accordance with the concepts of the invention, it is frequently desirable to adjust the pH of the resulting impregnant composition to insure the stability of the system and prevent precipitation of the silane from the solution. For this purpose, it is frequently desirable to formulate the impregnant composition to include a quaternary ammonium hydroxide to adjust the pH to the alkaline side.

The foregoing compositions can be applied to any of the fiber systems of the types described above whereby the vulcanization retarder containing in the impregnant composition serves to moderate the rate of vulcanization when the impregnated bundle is combined with elastomeric material in the manufacture of fiber reinforced elastomeric products. The use of such anchoring agent is particularly desirable in the case of glass fiber-reinforced elastomeric products since it is believed that the anchoring agents of the type described serve to intertie the impregnated bundle with the elastomeric material with which the bundle is combined.

It is desirable to achieve as full impregnation as possible into the bundles of fibers in order to more effectively separate the fibers one from the other by the impregnant. The deeper the penetration, the more effective will be the bond between the individual fibers in the bundle and the elastomeric material with which the bundles of fibers are combined in the subsequent manufacture of fiber reinforced elastomeric products.

In the final system, the elastomeric material with which the fiber bundle is combined will constitute a continuous phase, and it is believed that the tie-in between the impregnated bundles of fibers and the elastomeric material forming the continuous phase will occur primarily during cure or vulcanization of the elastomeric material during fabrication of the fiber reinforced elastomeric product.

In fabricating combinations of metal or synthetic fiber bundles prepared in accordance with the procedures of this invention with elastomeric materials, the bundles are admixed with the elastomeric material or otherwise laid down in the desired arrangement. The combination of the impregnated bundle and the elastomeric material or system is achieved in a conventional manner by molding or curing under heat and compression of the elastomeric material admixed with conventional accelerators, vulcanizing agents and/or other conventional processing aids in combination with the impregnated bundle whereby the bundle becomes securely integrated with the elastomeric material in the resultant product without the formation of the undesired elastomer-elastomer interface described above which serves to weaken the overall bond otherwise established between the impregnated fiber bundle and the elastomeric material when it is combined.

In accordance with the concepts of this invention, and as illustrated in FIG. 5 of the drawing, the glass fiber bundles 10 are thus integrated in the elastomeric material 11 forming the continuous phase without the formation of the elastomer-elastomer interface since the vulcanization retarders of this invention serve to moderate the rate of vulcanization of the elastomeric material immediately adjacent to the fiber bundles 10.

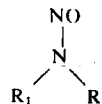
It will be understood that the concepts of the present invention are applicable to strands formed of a plurality of individual glass fiber filaments, and to cords formed of a plurality of strands which have been assembled or twisted together. Strands forming such cords may have a twist, a reverse twist or no twist at all in accordance with well known technology in the manufacture of glass fibers. In addition, the concepts of the invention are also applicable to woven and non-woven fabrics formed from cords of the type described above.

It will be understood that various changes and modifications can be made in the details of formulation, methods of application and use without departing from the spirit of the invention, especially as defined in the following claims.

I claim:

1. A glass fiber bundle formed of a plurality of glass fibers and an impregnant in the bundle, said impregnant containing an alkaline polymeric elastomer compatible material and containing an acidic vulcanization retarder capable of reaction with low molecular weight components of the elastomer compatible material, said retarder being an N-nitroso amine.

2. A fiber bundle as defined in claim 1 wherein the amine has the formula



wherein R_1 is aryl and substituted derivatives thereof and R_2 is selected from the group consisting of alkyl, cycloalkyl, aryl and substituted derivatives thereof.

3. A fiber bundle as defined in claim 1 wherein the retarder is present in the form of a thin coating on the impregnated bundle.

4. A fiber bundle as defined in claim 1 wherein the retarder is admixed with the elastomer compatible material.

5. A fiber bundle as defined in claim 1 wherein the elastomer compatible material is a mixture of an elastomer latex with an amine-modified resorcinol aldehyde resin.

6. A fiber bundle as defined in claim 1 wherein the elastomer compatible material is a butadiene-styrene-vinyl pyridine terpolymer.

7. A fiber bundle as defined in claim 1 wherein the elastomer compatible material is selected from the group consisting of urea-aldehyde resins, melamine-aldehyde resins, polyesters, polyamides and polyepoxides.

8. A fiber bundle as defined in claim 1 wherein the retarder is present in an amount within the range of 0.1 to 25 percent by weight based on the weight of the impregnant in the bundle.

9. A fiber bundle as defined in claim 1 wherein the impregnant includes an organo silicon anchoring agent.

10. A fiber bundle as defined in claim 1 wherein the fiber bundle is in the form of a cord formed of a plurality of strands of glass fibers.

11. A fiber bundle as defined in claim 10 wherein the strands forming the cords are twisted and plied together.

12. A fiber bundle as defined in claim 1 wherein the fiber bundle is in the form of a woven or non-woven fabric formed of fibers in the form of cords.

13. In a glass fiber-reinforced elastomeric product in which an elastomeric material constitutes a continuous phase in which bundles of glass fibers are distributed, the improvement in the bonding relationship between the glass fibers and the elastomeric material comprising an impregnated glass fiber bundle in which the impregnant is an alkaline, polymeric elastomer compatible material and contains an acidic vulcanization retarder capable of reaction with low molecular weight components of the elastomer compatible material in response to heat during cure or vulcanization, said retarder being an N-nitroso amine.

14. A product as defined in claim 13 wherein the amine has the formula



wherein R_1 is aryl and substituted derivatives thereof and R_2 is selected from the group consisting of alkyl, cycloalkyl, aryl and substituted derivatives thereof.

15. A product as defined in claim 13 wherein the retarder is present in the form of a thin coating on the impregnated bundle.

16. A product as defined in claim 13 wherein the retarder is admixed with the elastomer compatible material.

17. A product as defined in claim 13 wherein the elastomer compatible material is a mixture of an elastomer latex with an amine-modified resorcinol aldehyde resin.

18. A product as defined in claim 13 wherein the elastomer compatible material is a butadiene-styrene-vinyl pyridine terpolymer.

19. A product as defined in claim 13 wherein the elastomer compatible material is selected from the group consisting of urea-aldehyde resins, melamine-aldehyde resins, polyesters, polyamides and polyepoxides.

20. A product as defined in claim 13 wherein the retarder is present in an amount within the range of 0.1 to 25 percent by weight based on the weight of the impregnant in the bundle.

21. A product as defined in claim 13 wherein the impregnant includes an organo silicon anchoring agent.

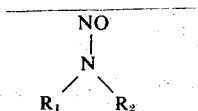
22. A product as defined in claim 13 wherein the fiber bundle is in the form of a cord formed of a plurality of strands of glass fibers.

23. A product as defined in claim 22 wherein the strands forming the cords are twisted and plied together.

24. A product as defined in claim 13 wherein the fiber bundle is in the form of a woven or non-woven fabric formed of fibers in the form of cords.

25. In the method for the manufacture of glass fiber-reinforced elastomeric products in which a bundle of impregnated fibers is combined with an elastomeric material and the resulting combination is molded under heat and pressure to integrate the glass fiber bundle in the elastomeric material, the improvement comprising providing at least a coating of an acid vulcanization retarder on a bundle impregnated with an alkaline, polymeric elastomer compatible material and molding the bundle with an elastomeric material under heat and pressure whereby a uniform rate of vulcanization or cure is achieved throughout the reinforced elastomeric product, said retarder being an N-nitroso amine.

26. A method as defined in claim 25 wherein the amine has the formula



wherein R_1 is aryl and substituted derivatives thereof and R_2 is selected from the group consisting of alkyl, cycloalkyl, aryl and substituted derivatives thereof.

27. A method as defined in claim 25 wherein the re-

tarder is admixed with the elastomer compatible material.

28. A method as defined in claim 25 wherein the elastomer compatible material is a mixture of an elastomer latex with an amine-modified resorcinol aldehyde resin.

29. A method as defined in claim 25 wherein the elastomer compatible material is a butadiene-styrene-vinyl pyridine terpolymer.

30. A method as defined in claim 25 wherein the elastomer compatible material is selected from the group consisting of urea-aldehyde resins, melamine-aldehyde resins, polyesters, polyamides and polyepoxides.

31. A method as defined in claim 25 wherein the impregnant includes an organo silicon anchoring agent.

32. A method as defined in claim 25 wherein the fiber bundle is in the form of a cord formed of a plurality of strands of glass fibers.

33. A method as defined in claim 32 wherein the strands forming the cords are twisted and plied together.

34. A method as defined in claim 25 wherein the fiber bundle is in the form of a woven or non-woven fabric formed of fibers in the form of cords.

35. A glass fiber bundle formed by a plurality of glass fibers and an impregnant in the bundle, said impregnant comprising an alkaline blend of a resorcinol-aldehyde resin and an elastomer and containing an acidic vulcanization retarder in the form of an N-nitroso amine having the formula



wherein R_1 is aryl and substituted derivatives thereof and R_2 is selected from the group consisting of alkyl, cycloalkyl, aryl and substituted derivatives thereof.

36. In a glass fiber reinforced elastomeric product in which an elastomeric material constitutes a continuous phase in which bundles of glass fibers are distributed, the improvement in the bonding relationship between the glass fiber bundle and the elastomeric material comprising an impregnated glass fiber bundle in which the impregnant is an alkaline blend of a resorcinol-aldehyde resin and an elastomer and contains an acidic vulcanization retarder in the form of an N-nitroso amine having the formula



wherein R_1 is aryl and substituted derivatives thereof and R_2 is selected from the group consisting of alkyl, cycloalkyl, aryl and substituted derivatives thereof.

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