



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: PCT/US93/11722 (22) International Filing Date: 3 December 1993 (03.12.93) (30) Priority Data: 07/985,781 4 December 1992 (04.12.92) US (71) Applicant: PPG INDUSTRIES, INC. [US/US]; One PPG Place, Pittsburgh, PA 15272 (US). (72) Inventor: KLETT, Michael, W.; 9499 Peebles Road, Allison Park, PA 15101 (US). (74) Agents: STACHEL, Kenneth, J.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al.</p>		<p>(81) Designated States: AU, BR, CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: CHEMICAL TREATMENT FOR GLASS FIBERS</p>		
<p>(57) Abstract</p> <p>An aqueous sizing for reinforced glass fibers provides improved processing properties, shear strength and compatibility with phenolic resin reinforcers. The coated, reinforced glass fibers are useful in filament winding and pultrusion wherein the coating is an aqueous sizing comprising a ureido-modified amino silane coupling agent and a polyvinyl pyrrolidone film-former. The sizing is free of epichlorohydrin-polyamide reaction products and vinyl aromatic monomer-maleic anhydride copolymers.</p>		

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CHEMICAL TREATMENT FOR GLASS FIBERSBACKGROUND OF THE INVENTION

This invention is directed to chemical treatments,  
5 called sizings, for glass fibers which are to be incorporated  
into resin systems for use as reinforcement or as a solid  
article.

Fibers, particularly glass fibers, are useful as  
reinforcement in a number of different applications such as  
10 described in the Fiberglass-Reinforced Plastics Deskbook by  
Nicholas P. Cheremisinoff and Paul N. Cheremisinoff, Ann  
Arbor Science Publishers, Inc., 1979, Library of Congress  
Catalog Card Number 78-62293. In combining glass fibers with  
various resins, it is important that the fibers have good  
15 processing properties like low fuzz production and good wet-  
out and wet-through. It is also important that the resulting  
product have high mechanical properties, particularly high  
shear strength.

One application of glass fibers is in filament  
20 winding. In filament winding, continuous glass fibers  
impregnated with resin are wound around a steel mandrel until  
a desired thickness is reached. The resin used depends on  
the properties desired in the end product, and the sizing for  
the glass fibers depends on the resin system which is used.  
25 Useful resins for this process are the liquid phenolic  
resins.

Another use for glass fibers is in the process of  
pultrusion. In pultrusion, a plurality of glass fibers are  
pulled through a heated die where they are combined with  
30 resin. As the resin and glass pass through the die, the heat  
cures the resin thereby forming a solid article. A common  
example of a pultruded article is the side rail of step  
ladders. These are easily recognizable since they are

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generally a bright color, like orange. Liquid phenolic resins are also particularly useful in pultrusion processes.

It is an object of this invention to provide sized fibers which provide desirable processing and mechanical  
5 properties in pultrusion and filament winding applications, and that show good compatibility with phenolic resins.

#### SUMMARY OF THE INVENTION

The objects of the invention are achieved by glass  
10 fibers having thereon a sizing which is applied in an aqueous state and then dried. This sizing has, in addition to water, a ureido modified amino silane coupling agent, a polyvinyl pyrrolidone film former, and a cationic lubricant. The sizing may optionally have additional silane coupling agents,  
15 lubricants, film formers and plasticizers though it is preferred that the sizing be essentially free of components such as epichlorohydrin polyamide reaction products or copolymers of a vinyl aromatic monomer and maleic anhydride.

#### DETAILED DESCRIPTION OF THE INVENTION

Glass fibers employed in the invention may be those such as "E glass", "S glass", "D glass" or any of the glasses known in the art. Typical formulations of such glass fibers are disclosed in The Manufacturing Technology of  
25 Continuous Glass Fibres, Library of Congress Catalog Card Number 72-97429, by K. L. Loewenstein, Elsevier Scientific Publishing, 1973, at page 29.

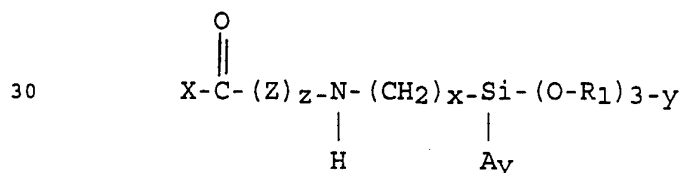
The aqueous sizing composition is applied by sprayers, rollers, belts, or the like. The sized glass  
30 fibers are gathered into bundles comprising a plurality of individual fibers, generally from 200 to more than 3000. The bundles are usually wound onto a forming package and the sizing is dried at room temperature or by oven heating for a

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time and at a temperature which will remove the moisture from the fibers. The preferred time/temperature relationship for the sizing of this invention is about 285°F (141°C) for about 10 hours. The sized glass fibers generally have between  
 5 about 0.05 and 5 percent of sizing composition based on the weight of the glass fiber.

The sizing of this invention can have, in addition to water, 10 to 35 weight percent on a non-aqueous basis of ureido modified amino silane coupling agent, 25 to 70 weight  
 10 percent on a non-aqueous basis of polyvinyl pyrrolidone homopolymer film former, and 5 to 25 weight percent on a non-aqueous basis of cationic lubricant. The sizing may also have 0 to 15 weight percent on a non-aqueous basis of  
 15 additional silane coupling agents (though preferably the amount of additional silane present is greater than zero) such as amino functional and epoxy functional silanes. The sizing may also have other lubricants and film formers, and 0  
 20 to 35 weight percent on a non-aqueous basis of plasticizers (though preferably the amount of plasticizer present is greater than zero) for the polyvinyl pyrrolidone film former, provided, however, that there be at least one part polyvinyl  
 pyrrolidone to each part plasticizer on a weight basis.

By "ureido modified silane" is meant the novel ureido functional silanes of U.S. Patents Nos. 3,754,971 and  
 25 4,626,560 or an amino functional silane of the following general formula:



5 wherein; X is  $\begin{matrix} -N-R_2, & \begin{matrix} (CH_2)_v \\ / \quad \backslash \\ -N---C=O \end{matrix} & \text{or} & -O-(CH_2)_w-CH_3 \\ | \\ R_3 \end{matrix}$

10 Z is  $\begin{matrix} -R_4-N-R_5- \\ | \\ H \end{matrix}$

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> may each independently be H, or an alkyl group;

A is an alkyl or alkoxide group;

15 v is an integer from 1 to 10;

w is an integer from 0 to 10;

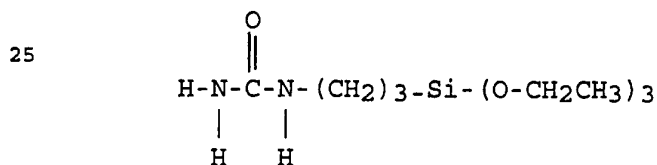
x is an integer from 1 to 10;

y is an integer from 0 to 3;

z is either 0 or 1;

20 and Si is a silane atom, C a carbon atom, O an oxygen atom, N a nitrogen atom and H a hydrogen atom.

The preferred silane is defined by the formula:



30 which is sold in a 50 percent solution in methanol as A-1160 by Union Carbide Corporation. Such silanes may be used in the unhydrolyzed, partially hydrolyzed or hydrolyzed form. Hydrolysis of silanes is accomplished by contact with organic acid, preferably acetic acid.

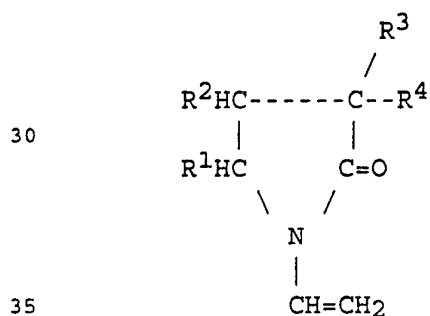
35 Polyvinyl pyrrolidone is the main film former though additional film formers may be used which are water

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soluble, dispersible or emulsifiable, such as starches and polyvinyl alcohols.

Starches which may be used include amylose-containing starches and starch mixtures derived from any starch sources including corn, wheat, potato, tapioca, waxy maize, sago, rice, hybrid starches, etc. Conventionally, however, the starch components having a high amylose content, e.g. 50 to 60 percent by weight, are derived from either corn starch or a hybrid corn starch. The starch components having a low amylose content, e.g. 20 to 30 percent by weight are usually derived from either potato or derivatized corn starch, such as cationic, phosphatized, ethoxylated or etherified derivatives. The overall amylose content of a starch mixture can vary from about 35 to about 55 percent by weight based on the total starch content. Examples of suitable starches are those of U.S. Patent Nos. 3,227,192; 3,265,516; and 3,887,389. An example of commercially available starches which may be suitable for this invention are "Hylon", sold by National Starch and Chemical Co., and "Amaizo 2213" sold by American Maize Products Company.

Polyvinyl pyrrolidone is the key film former. By the term "polyvinyl pyrrolidone" is meant any homopolymer obtained by the addition polymerization of a monomer which may be represented by the formula:



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wherein R1, R2, R3 and R4 may each be hydrogen or lower alkyls. Examples of such monomers include N-vinyl-2-pyrrolidone, 5-methyl-N-vinyl-2-pyrrolidone,  
5 4-methyl-N-vinyl-2-pyrrolidone, 5-ethyl-N-vinyl-2-pyrrolidone, 4-ethyl-N-vinyl-2-pyrrolidone, 3-methyl-N-vinyl-2-pyrrolidone, 3-ethyl-N-vinyl-2-pyrrolidone, 3,3-dimethyl-N-vinyl-2-pyrrolidone, 3,5-dimethyl-N-vinyl-2-pyrrolidone and the like. These  
10 monomers and their homopolymerization products are known in the art. It is preferred that the polyvinyl pyrrolidone have an average molecular weight of from about 5000 to 100,000. Suitable polyvinyl pyrrolidones produced by the polymerization of N-vinyl-2-pyrrolidone are available from  
15 International Specialty Products under the trade designations PVP K-15, PVP K--0, PVP K-60 and PVP K-90 wherein the K-value identifies the viscosity grade. The number average of the molecular weights for these grades is about 10,000, 40,000, 160,000 and 360,000, respectively.

20 A plasticizer may also be present for the polyvinyl pyrrolidone film former. Examples of suitable plasticizers for polyvinyl pyrrolidone are carboxymethylcellulose, cellulose acetate, polyoxyalkylene glycols, glycerin, dimethyl phthalate, diethylene glycol,  
25 dibutyl tartrate, and polyalkylene glycols. The preferred plasticizer is polyethylene glycol, examples of which are available from Union Carbide Corporation under the product designations Carbowax 300 and Carbowax 400 having approximate molecular weights of 300,000 and 400,000, respectively.

30 While essentially any cationic lubricant known in the art may be used, the preferred cationic lubricants are alkyl imidazoline derivatives. These include compounds of the class n-alkyl-N-amido-alkyl imidazolines, which may be



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formed by causing fatty acids or carboxylic acids to react with polyalkylene polyamines under conditions which produce ring closure. The reaction of tetraethylene-pentamine with stearic acid is exemplary of such a reaction and the product is available under the name Cation-X<sup>®</sup> from Lyndal Chemical Co. These imidazolines are described in U.S. Patent No. 2,200,815 and other imidazolines are described in U.S. Patent Nos. 2,267,965; 2,268,273; and 2,353,837.

Other cationic lubricants which may be used alone or in combination with the alkyl imidazoline derivative include a polyamino functional polyamide resin formed normally by the condensation reaction of a polycarboxylic acid such as tetraethylene pentamine, ethylene triamine, diethylene triamine, diethylenetetramine and the like. One such resin is Versamid 140 which has an amine value of 370 to 400 and is available from General Mills. Another useful cationic lubricant is the partially amidated polyamine having the trade designation Emery<sup>®</sup> 6717 available from Henkel Corp.

Additional silane coupling agents may be included in the sizing utilized in this invention and include amino functional silanes like those having the formula  $\text{NH}_2\text{-R}_2\text{-Si(OR}_1\text{)}_z$  where  $z$  is an integer from 1 to 3.  $\text{R}_1$  can be the same or different moieties selected from lower alkyl or aliphatic hydrocarbons having less than eight and preferably less than 5 carbon atoms, and  $\text{R}_2$  is a difunctional radical selected from the lower alkyl or aliphatic hydrocarbons having less than eight carbon atoms. The corresponding hydrolysis products can also be employed, such as the corresponding silanols and/or polysiloxanes. Amino functional silanes of the general type gamma-aminoalkyltrialkoxo silane may be used. Examples of such additional silane coupling agents include gamma-aminopropyltriethoxy silanes such as those commercially

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available from Union Carbide Corporation under the trade designation A-1100 silane coupling agent and A-1108 amino silane coupling agent which is modified with a lubricant. Epoxy functional silanes of the general type gamma-  
5 glycidoxyalklytrialkoxo silane such as gamma-glycidoxypropyltrimethoxy silane, commercially available as Union Carbide's A-187, are also useful.

While other ingredients may be added to the composition of this invention, the sizing is essentially free  
10 of epichlorohydrin polyamide reaction products and copolymers of a vinyl aromatic monomer and maleic anhydride.

The resin which may be used with fibers sized as disclosed above are those of the liquid phenolic type. By "liquid phenolic" resins what is meant is those resins which  
15 are formed by the condensation reaction of phenols and aldehydes. Such resins are well known in the art and are described in Polymer Synthesis, by Stanley R. Sandler and Wolf Karo, volume II, chapter 2, by Academic Press, Inc., New York, NY., 1977, Library of Congress Catalog Card Number  
20 73-2073, which is part of the series Organic Chemistry: A Series of Monographs, Volume 29. In the condensation reaction, in addition to phenol, other phenols such as o-cresol, mixed cresols, p-tert-butylphenol, p-phenylphenol, resorcinol and cardanol may be used. Aldehydes such as  
25 formaldehyde and furfural may be used.

Examples of sizings according to this invention are shown in Table I and all of the ingredients appearing in Table I have been described above.

Table I

Ingredient	A		B		C		D	
	g/g	%	g/g	%	g/g	%	g/g	%
5 PVP K-15	82.5	32	0	0	0	0	0	0
PVP K-30	0	0	70	27	107	38.5	107	39.6
Carbowax 300	70	27	0	0	0	0	0	0
Carbowax 400	0	0	56.5	22	11	4	11	4
10 Hylon starch	0	0	26	10	40	14	40	15
A-1100	29	11	29	11	32	11.5	0	0
A-1160	53	20.4	53	20.4	59	21	59	22
A-187	0	0	0	0	0	0	24	9
Cation X <sup>®</sup>	25	9.6	25	9.6	25	9	25	9.3
15 Versamid 140	0	0	0	0	4	1.4	4	1.5

Units are grams per gallon and percentages are by weight on a non-aqueous basis.

20 The preparation of sizings is well known in the art and the procedure which follows is one example of the several appropriate procedures which can be employed. The procedure for preparing the above sizings is similar and the following illustrates the preparation of example A above.

25 1200 grams of hot (120-160°F or 49-71°C) water were added to a main mix tank; the polyvinyl pyrrolidone was slowly added to the main mix tank with stirring; Carbowax 300 polyethylene glycol was dissolved in hot water and added to the main mix tank; 1000 grams of hot water were added to a second tank; 29

30 grams of A-1100 silane and 53 grams of A-1160 silane were added to the second tank with stirring and then transferred to the main mix tank; Cation-X<sup>®</sup> lubricant was dispersed in hot water and then added to the main mix tank.

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Fibers sized with the solution of example C were pultruded with a liquid phenolic resin. The fibers were E-glass of "K" diameter or approximately 13 microns in diameter. The fibers were sized using a roller applicator and were dried in an oven at 285°F (141°C) for 10 hours. The liquid phenolic resin used was a mixture of 74 percent resorcinol-formaldehyde resin and 26 percent phenol/polymer with paraformaldehyde (phenol-formaldehyde condensate). Both resin products are sold commercially by Indspec Chemical Corporation of Pittsburgh, PA and are designated Resorciphen™ 2026-B resin and Resorciphen™ 2074-A resin respectively. The pultrusion die was maintained at a temperature of about 375-400°F (195-205°C) and the glass fibers and resin moved at about 12 inches (305 cm) per minute through the die. The final product had about 72-75 weight percent glass. The product had a short beam shear strength according to ASTM test No. D-2344 of 5.45 Kpsi and a flexural strength according to ASTM test No. D-790 of 128.8 Kpsi.

Fibers sized with the solution of example A were filament wound with liquid phenolic resin. The fibers were E-glass of "T" diameter or about 23.5 microns. The fibers were sized and dried as described above. The resin was a mixture of phenol-formaldehyde types produced by Indspec Chemical Corporation under the trade designations PRF2 1000 and PRF2 1030FM. The glass fibers with the resin were filament wound in the manner known in the art at a 54° wind angle to produce a 2 inch (51 cm) diameter pipe with a wall thickness of 0.1 inches (2.5 mm) using three complete layers of glass fibers which had a yield of 250 yards/lb. The pipe was cured by heating for 2 hours at between 70 and 80°C and then for 90 minutes at 90°C. The same procedure was used to produce a similar pipe using the same resin but using a different, commercially available, competitive glass fiber.

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The commercially available glass was E-glass of approximately 23 microns in diameter. Both pipe samples were subjected to destructive crush testing to determine the point of failure. The competitive glass fiber pipe failed at a load of 262  
5 pounds while the pipe made with the fibers sized according to example A failed at a load of 393 pounds, or about 50 percent greater.

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I claim:

1. A glass fiber coated with a dried residue of an aqueous sizing, where the sizing comprises:
  - 5 (a) an unhydrolyzed, partially hydrolyzed or hydrolyzed ureido modified amino silane coupling agent;
  - (b) a polyvinyl pyrrolidone homopolymer film former;
  - 10 (c) at least one cationic lubricant;
  - (d) water in an amount to provide an aqueous solution for coating the fiber wherein the sizing is essentially free of epichlorohydrin polyamide reaction products and copolymers of a vinyl aromatic monomer and maleic anhydride.
  - 15
2. The glass fiber of claim 1 further comprising a plasticizer in the aqueous sizing, provided, however, that there be at least one part polyvinyl pyrrolidone to each part  
20 plasticizer on a weight basis.
3. The glass fiber of claim 2 wherein the plasticizer is polyethylene glycol.
- 25 4. The glass fiber of claim 1 further comprising at least one additional silane in the aqueous sizing.
5. The glass fiber of claim 4 wherein the silane is selected from the group consisting of amino functional  
30 silanes and epoxy functional silanes and mixtures thereof.
6. The glass fiber of claim 4 wherein the silane is selected from the group consisting of gamma-

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glycidoxypropyltrimethoxysilane and gamma-aminopropyltriethoxysilane and mixtures thereof.

7. The glass fiber of claim 1 further comprising  
5 a polyamino functional polyamide resin in the aqueous sizing.

8. The glass fiber of claim 1 wherein the cationic lubricant is selected from the group consisting of alkyl imidazoline derivatives and fatty imidazoline  
10 derivatives of tetraethylene-pentamine and stearic acid.

9. A glass fiber coated with a dried residue of an aqueous sizing, where the sizing comprises:

(a) 10 to 35 weight percent on a  
15 non-aqueous basis of an unhydrolyzed, partially hydrolyzed or hydrolyzed ureido modified amino silane;

(b) 0 to 15 weight percent on a non-aqueous basis of silane selected from the group consisting of amino functional silanes and epoxy functional  
20 silanes and mixtures thereof;

(c) 5 to 25 weight percent on a non-aqueous basis of cationic lubricant selected from the group consisting of alkyl imidazoline derivatives and fatty imidazoline derivatives of  
25 tetraethylene-pentamine and stearic acid;

(d) 25 to 70 weight percent on a non-aqueous basis of polyvinyl pyrrolidone homopolymer film former;

(e) 0 to 35 weight percent on a non-aqueous  
30 basis of polyethylene glycol, provided, however that there be at least one part polyvinyl

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pyrrolidone to each part polyethylene glycol on a weight basis, and;

(f) water in an amount to provide an aqueous solution for coating the fiber wherein the sizing is essentially free of epichlorohydrin polyamide reaction products and copolymers of a vinyl aromatic monomer and maleic anhydride.

10. A phenolic resin reinforcing fiber coated with a dried residue of an aqueous sizing composition, where the sizing composition comprises:

(a) an unhydrolyzed, partially hydrolyzed or hydrolyzed ureido modified amino silane coupling agent;

(b) a polyvinyl pyrrolidone homopolymer film former;

(c) at least one cationic lubricant;

(d) water in an amount to provide an aqueous solution for coating the fiber wherein the sizing is essentially free of epichlorohydrin polyamide reaction products and copolymers of a vinyl aromatic monomer and maleic anhydride.

11. The phenolic resin reinforcing fiber of claim 10 further comprising a plasticizer in the aqueous sizing, provided, however, that there be at least one part polyvinyl pyrrolidone to each part plasticizer on a weight basis.

12. The phenolic resin reinforcing fiber of claim 11 wherein the plasticizer is polyethylene glycol.



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13. The phenolic resin reinforcing fiber of claim 10 further comprising at least one additional silane in the aqueous sizing.

5           14. The phenolic resin reinforcing fiber of claim 13 wherein the silane is selected from the group consisting of amino functional silanes and epoxy functional silanes and mixtures thereof.

10           15. The phenolic resin reinforcing fiber of claim 13 wherein the silane is selected from the group consisting of gamma-glycidoxypropyltrimethoxysilane and gamma-aminopropyltriethoxysilane and mixtures thereof.

15           16. The phenolic resin reinforcing fiber of claim 10 further comprising a polyamino functional polyamide resin in the aqueous sizing.

20           17. The phenolic resin reinforcing fiber of claim 10 wherein the cationic lubricant is selected from the group consisting of alkyl imidazoline derivatives and fatty imidazoline derivatives of tetraethylene-pentamine and stearic acid.

25           18. A phenolic resin reinforcing glass fiber coated with a dried residue of an aqueous sizing, where the sizing comprises:

- 30           (a) 10 to 35 weight percent on a non-aqueous basis of an unhydrolyzed, partially hydrolyzed or hydrolyzed ureido modified amino silane;
- (b) 0 to 15 weight percent on a non-aqueous basis of silane selected from the group consisting

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of amino functional silanes and epoxy functional silanes and mixtures thereof;

5 (c) 5 to 25 weight percent on a non-aqueous basis of cationic lubricant selected from the group consisting of alkyl imidazoline derivatives and fatty imidazoline derivatives of tetra-ethylene-pentamine and stearic acid;

10 (d) 25 to 70 weight percent on a non-aqueous basis of polyvinyl pyrrolidone homopolymer film former;

15 (e) 0 to 35 weight percent on a non-aqueous basis of polyethylene glycol, provided, however that there be at least one part polyvinyl pyrrolidone to each part polyethylene glycol on a weight basis, and;

20 (f) water in an amount to provide an aqueous solution for coating the fiber wherein the sizing is essentially free of epichlorohydrin polyamide reaction products and copolymers of a vinyl aromatic monomer and maleic anhydride.

19. A phenolic resin reinforcing glass fiber coated with a dried residue of an aqueous sizing, where the sizing comprises:

25 (a) 15 to 25 weight percent on a non-aqueous basis of an unhydrolyzed, partially hydrolyzed or hydrolyzed ureido modified amino silane;

30 (b) 5 to 15 weight percent on a non-aqueous basis of silane selected from the group consisting of amino functional silanes and epoxy functional silanes and mixtures thereof;

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(c) 5 to 15 weight percent on a non-aqueous basis of cationic lubricant selected from the group consisting of alkyl imidazoline derivatives and fatty imidazoline derivatives of tetra-  
5 ethylene-pentamine and stearic acid;

(d) 25 to 50 weight percent on a non-aqueous basis of polyvinyl pyrrolidone homopolymer film former;

(e) 20 to 35 weight percent on a non-  
10 aqueous basis of polyethylene glycol, provided, however that there be at least one part polyvinyl pyrrolidone to each part polyethylene glycol on a weight basis, and;

(f) water in an amount to provide an  
15 aqueous solution for coating the fiber wherein the sizing is essentially free of epichlorohydrin polyamide reaction products and copolymers of a vinyl aromatic monomer and maleic anhydride.

20 20. A phenolic resin reinforcing glass fiber coated with a dried residue of an aqueous sizing, where the sizing comprises:

(a) 15 to 25 weight percent on a  
25 non-aqueous basis of an unhydrolyzed, partially hydrolyzed or hydrolyzed ureido modified amino silane;

(b) 5 to 15 weight percent on a non-aqueous  
30 basis of silane selected from the group consisting of gamma-aminopropyltriethoxy-silane and gamma-glycidoxypropyltri-methoxysilane and mixtures thereof;

(c) 5 to 15 weight percent on a non-aqueous basis of cationic lubricant selected from the

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group consisting of alkyl imidazoline derivatives and fatty imidazoline derivatives of tetra-ethylene-pentamine and stearic acid;

5 (d) 25 to 50 weight percent on a non-aqueous basis of polyvinyl pyrrolidone homopolymer film former;

(e) 20 to 35 weight percent on a non-aqueous basis of polyethylene glycol, provided, however that there be at least one part  
10 polyvinyl pyrrolidone to each part polyethylene glycol on a weight basis, and;

(f) water in an amount to provide an aqueous solution for coating the fiber wherein the sizing is essentially free of epichlorohydrin  
15 polyamide reaction products and copolymers of a vinyl aromatic monomer and maleic anhydride.

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/11722

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC(5) :B32B 17/02, 17/04  
 US CL :428/383, 391  
 According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**  
 Minimum documentation searched (classification system followed by classification symbols)  
 U.S. : 428/383, 391; 524/514, 548; B32B 17/02, 17/04; CO8K 3/20, 7/14, 9/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 USPTO APS AND ORBIT-DERWENT (SILANES, GLASS FIBERS AND POLYVINYL PYRROLIDONE)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,810,576 (GAA ET AL.) 07 March 1989 , see column 9, lines 21-23; column 6, lines 59-60 and column 10, lines 41-49.	1-3,8 & 9
X	US, A, 4,795,678 (GIRGIS) 03 January 1989, see column 8, lines 59-67; column 1, line 52 and column 3, lines 57-62.	1-3, 8 & 9
Y	US, A, 3,249,411 (McWILLIAMS ET AL.) 03 May 1966, column 2, line 10 and column 3, lines 12-24.	1-3, 8 & 9
Y	JP, A, 3-294337 (ASAHI FIBER GLASS KK) 25 December 1991.	1-3, 8 & 9

Further documents are listed in the continuation of Box C.  See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 01 FEBRUARY 1994	Date of mailing of the international search report 19 MAY 1994
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Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer <i>Robert Sellers for</i> ROBERT SELLERS Telephone No. (703) 308-2351
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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/11722**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:  
1-3, 8 and 9

Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

**BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING**

This ISA found multiple inventions as follows:

- I. Claims 1-3, 8 and 9, drawn to an aqueous sizing coated on a glass fiber, classified in class 428 subclass 391.
- II. Claims 4-6, drawn to the coated glass fiber wherein the aqueous sizing further comprises an additional silane, classified in class 428 subclass 391.
- III. Claim 7, drawn to the coated glass fiber wherein the aqueous sizing further comprises a polyamino-functional polyamide, classified in class 428 subclass 391.
- IV. Claims 10-12, 17 and 18, drawn to a phenolic resin-reinforced glass fiber coated with an aqueous sizing, classified in class 428 subclass 383.
- V. Claims 13-15, 19 and 20, drawn to a phenolic resin-reinforced glass fiber coated with an aqueous sizing further comprising an additional silane, classified in class 428 subclass 383.
- VI. Claim 16, drawn to a phenolic resin-reinforced glass fiber coated with an aqueous sizing further comprising a polyamino-functional polyamide, classified in class 428 subclass 383.

These groups lack unity of invention for the following reasons:

The intermediate of Group I does not have the same essential structural elements as the final products of Groups II-VI in that the basic chemical structure of the intermediate without the additional amino or epoxy-functional silane (Groups II and V), phenolic resin (Groups II-VI) and/or polyamino-functional polyamide (Groups III and VI) is not the same as the final products of Groups II-VI. The diverse functionalities and chemical structures of the reactants in the final products yield chemically distinct sized glass fibers from the intermediate. Therefore, the intermediate of Group I and the final products of Groups II-VI do not form a single inventive concept due to the different special technical features with respect to the chemically and structurally distinct reactants which compose the final products in comparison to the intermediate.