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(21) International Application Number: PCT/US93/06227 (22) International Filing Date: 30 June 1993 (30.06.93) (30) Priority data: 912,559 13 July 1992 (13.07.92) US (71) Applicant: OWENS-CORNING FIBERGLAS CORPORATION [US/US]; 26 Fiberglas Tower 26, Toledo, OH 43659 (US). (72) Inventors: COSSEMENT, Marc ; Rue du Bay-Bonnet 28, B-4620 Fleron (BE). MASSON, Nadia ; Rue Chapelle à la Lice 25B, B-4621 Retinne (BE). PIRET, Willet ; Rue Falhez 53, B-4652 Xhendelesse (BE).		(74) Agents: GILLESPIE, Ted, C. et al.; Fiberglas Tower 26, Toledo, OH 43659 (US). (81) Designated States: JP, KR, European patent (DE, ES, FR, GB, IT). Published <i>With international search report.</i>
(54) Title: SIZE COMPOSITION (57) Abstract An aqueous coating composition comprising a polyurethane/isocyanate emulsion, a homopolymer of acrylic acid, an amino silane and water. The sizes are particularly useful for reinforcing polyamide resins (nylons).		

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DESCRIPTION
SIZE COMPOSITION

TECHNICAL FIELD

10 This invention relates to a size composition, coated glass fibers and reinforced thermoplastics. These sizes are particularly useful for reinforcing polyamide resins (nylons).

BACKGROUND ART

15 Numerous thermoplastic materials are available including polyolefins, polyacetals, polyamides (nylons), polycarbonates, polystyrenes, styrene-acrylonitrile copolymers, acrylonitrile-butadiene styrene (ABS) copolymers and polyvinyl chloride (PVC). Thermoplastic resin and glass fibers are made into useful shapes by means of heat and pressure. Processes include injection
20 of hot resin into a mold, extrusion and pultrusion. Other processes include hot calendaring, casting, vacuum forming and the like. Chopped glass fibers feed into these processes to strengthen and stiffen the resulting composite.

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DISCLOSURE OF THE INVENTION

 The invention includes a size consisting essentially of:

 a polyurethane/isocyanate emulsion containing blocked isocyanates;

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 a homopolymer of acrylic acid monomer;

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one or more amino organo-silane coupling agents; and

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water.

In the preferred embodiment, we also add polyvinyl pyrrolidone (PVP) for better strand integrity, size stability and fuzz reduction.

10 The resulting coated glass fibers yield desirable reinforced thermoplastics. We have found an especially surprising effect on the processability of the reinforcements without any sacrifice in mechanical properties for reinforced nylon in the case of aging in a water/ethylene glycol medium.

BEST MODE OF CARRYING OUT INVENTION

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The glass size composition of the present invention is useful with filamentous glass which is well known to those skilled in the art. Various types of glass filaments, such as "E" glass and other known types of glass, can be sized with the size. The size is useful on glass filaments having a wide range of diameters and
20 can be used on glass filaments whether or not they are gathered into fibers, ropes, rovings, yarns and the like.

Various polyurethane dispersions which are useful in the present invention include aqueous emulsions of blocked polyurethane resins such as aqueous solutions
25 of polyurethane polymers formed by a reaction between an organic isocyanate or polyisocyanate and an organic polyhydroxylated compound or hydroxyl terminated polyether or polyester polymer. The polyurethane dispersion may contain a crosslinking group.

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Other suitable examples include chain extended thermoplastic polyurethanes derived from chain extension of an isocyanate-terminated prepolymer prepared by the reaction of an aliphatic or cycloaliphatic diisocyanate with a polyalkylene ether polyol. A suitable polyurethane emulsion is Rucothane latex having a trade designation of 2011L available from Ruco Chemical Corp. from New York. This material along with other Rucothane polyurethane lattices are thermoplastic polyurethane lattices comprised of high molecular weight aliphatic isocyanate-based thermoplastic elastomers in a water dispersion with an anionic or nonionic surfactant, where the dispersion or latex has varying particle sizes. The lattices typically have a polymer solids content ranging from around 55 to 65 percent by weight where the urethane polymer has an ester backbone.

Other suitable polyurethane dispersions include:

- . From Bayer: PU402
- . From Baxenden: BW 197-58X
- . From Witco: 290H
- . From Hooker: Ruco 2010 L
- . From Synthomer: Vondic 2220

The preferred polyurethane is Baxenden 199-76X.

One suitable polyurethane crosslinking agent dispersion is an anionic aliphatic low branched polyester based polyurethane emulsion containing caprolactam

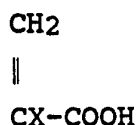
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blocked isocyanate which enables the polyurethane polymer to be cured at a temperature exceeding about 150°C. The polyurethane/crosslinking agent system has a milky white appearance having a percent solids of 60, an anionic particle charge of pH at 25°C of 8.0, and a viscosity at 25° Brookfield RVT of 150 cps. Specifically, one suitable polyurethane crosslinking agent dispersion comprises an aqueous dispersion of a high molecular weight branched polyurethane polymer based on polyester polyol and 1,1- methylenebis(isocyanatocyclohexane) wherein some of the polymer chains are terminated with blocked isocyanate groups. Other suitable polyurethane crosslinking agent dispersions comprise polyurethane/isocyanate emulsions of an aliphatic polyurethane containing blocked isocyanate having a milky white appearance, a percent solids of 40, a pH at 25°C of approximately 8-9, and a viscosity at 25°C Brookfield RVT of approximately 200-250 cps. Other suitable polyurethane crosslinking agent dispersions comprise a polyurethane and a trimer of 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate ("isophorone diisocyanate" or "IPDI") blocked with butanone oxime.

Other blocking groups like phenols, cresols Σ-caprolactam, malonates, aceto acetates, sodium bisulfite also may be used.

The acrylic acid monomer has the formula:

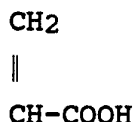


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wherein X is a hydrogen atom or a methyl or an
alkyl group having 1 to 10 carbon atoms.. Preferably,
5 the acrylic acid monomer has the formula:



The salt of the polyacrylic acid may be that of
10 alkalimetal or ammonium salts either derived from
ammonium hydroxide or from any organic primary, secondary
or tertiary amine poly- or monofunctionalized, e.g.
triethylamine, triethanolamine, glycine,
dimethylaminoethylmethacrylate. Degree of neutralization
of the polyacrylic acid may vary from about 20% to 90%.
15 Below 20%, the shelf life of the polyacrylic acid silane
mixture is too short and does not present industrial
interest. Preferred salts are those from ammonium
hydroxide with a degree of neutralization of about 40%.
Generally the ammonium hydroxide is added to the
polyacrylic acid aqueous solution in order to reach a pH
20 of about 5 or higher if it is necessary to adjust the pH
of the polyacid solution with the pH of the polyurethane
dispersion.

Some commercially available polyacrylic acid
homopolymers that have been evaluated successfully are
25 now given as example:

Acrylic acid homopolymer solutions:

(1) From Allied Colloid (UK)

30 . VERSICOL E5: Active content 25%; pH 1.5;
specific gravity 1.10;

viscosity 16 cps (25%);
approximate Mw 3,500.

5 . VERSICOL E7: Active content 25%; pH 1.5;
specific gravity 1.10;
viscosity 50 cps (25%);
approximate Mw 30,000.

10 . VERSICOL E9: Active content 25%; pH 1.5;
specific gravity 1.10;
viscosity 200 cps (25%);
approximate Mw 75,000.

. ANTIPREX 461: Active content 50%; pH 3.0;
specific gravity 1.26;
viscosity 600 cps (25%).

15 . DISPEX A40: Ammonium salt; active
content 40%; pH 7.5 - 8.5;
specific gravity 1.16.

. SYNCOL F40: Active content 40%; pH 2 - 2.5; viscosity 3.0 cS (5%, 25°C).

20 (2) From Rohm and Haas

. Acrysol A-1, Acrysol A-3, Acrysol A-5

TYPICAL PHYSICAL PROPERTIES			
	ACRYSOL A-1	ACRYSOL A-3	ACRYSOL A-5
Solids content, %	25	25	12.5
pH (5% aqueous solution)	about 2	about 2	about 2
Dilutability with Water	infinite	infinite	infinite
Molecular weight	~60,000	~190,000	~400,000
Viscosity (Brookfield), cps @25°C	15	18	20
5% solids content	15	65	260
12.5% solids content	160	1,550	-
25% solids content			

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. Acrysol LMW-10, Acrysol LMW-20, Acrysol LMW-

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Typical properties of ACRY SOL Polymers

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PRODUCT	FORM	MOLECULAR WEIGHT ²		Z TOTAL SOLIDS	DENSITY 25°C LBS/GAL	pH	BROOKFIELD VISCOSITY 25°C cps
		Mw	Mn				
ACRY SOL LMW-45	Partial Na Salt, 20% neutralized	4,500	3,000	48	10.2	4.0	800
ACRY SOL LMW-20	Partial Na Salt, 20% neutralized	2,000	1,425	48	10.3	4.0	185
ACRY SOL LMW-10	Partial Na Salt, 20% neutralized	1,000	750	48	10.5	4.0	45

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(3) From BF GOODRICH

. Good-Rite K732, Good-Rite K752

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Good-rite U\Polymers Appearance	<u>K-752</u>	<u>K-732</u>
	Hazy to Clear Amber Solution	Hazy to Clear Amber Solution
Molecular Weight	2,100	5,100
Total solids (%)	63	50
Sodium ion content (%)	0.79	0.48
pH (as shipped)	2.2-3.0	2.2-3.0
pH (1% aqueous solution)	3.1	2.8
Percent neutralization (weight %)	4.9	3.4
Specific gravity (g/cc)	1.23	1.18
Viscosity, cP at 25°C	400-1400	250-500
Surface tension (dyne/cm) (5% solution, pH 10)	59.1	62.9

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Particularly suitable organo-silane coupling agents include amino silanes such as gamma-aminopropyltriethoxysilane, available as A-1100 from Union Carbide. In various embodiments, the coupling agent can optionally further include additional, conventionally known aminosilanes such as gamma-methacryloxypropyltri-methoxy silane and/or a diamino silane such as N-beta-(aminomethyl)-gamma-amino propyltrimethoxysilane and triamino silanes.

The aqueous sizing compositions of the invention can be prepared following generally accepted mixing practices. These sizing compositions can be applied to the glass fiber using any convenient method. The amount of aqueous sizing composition applied is not narrowly critical, but is preferably controlled so as to deposit on the glass fibers a size coating comprising the dried residue of the aqueous sizing composition of the invention in an amount from about 0.25 to about 2 percent of the weight of the glass, taking into account the dilution of the non-volatile components in the aqueous sizing composition and the usual mechanical loss of some of the aqueous composition initially applied to the fibers before it is dried.

The aqueous sizing composition can be applied to the glass fibers drawing the fibers over a roll, pad, or other suitable surface wet or flooded with the aqueous sizing composition, by spraying, by dipping, or by any other suitable means. The overall concentration of the non-volatile components in the aqueous sizing composition can be adjusted over a wide range according to the means

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of application to be employed, the character of the glass
 fibers to be sized, e.g., their diameter and composition,
 5 and the weight of dried size coating desired for the
 intended use of the sized fibers.

Generally, the size composition has the
 following composition in parts per 100 parts of solids:

	parts per 100 <u>parts of solids</u>
10 polyurethane/isocyanate	5 to 80
emulsion	
homopolymer of acrylic acid	20 to 90
amonium hydroxide	to pH 5 - 11
amino silane	3 to 50
15 water	balance

Preferably, the size composition ranges has the
 following formulation:

	parts per 100 <u>parts of solids</u>
polyurethane/isocyanate	20 to 60
20 emulsion	
homopolymer of acrylic acid	30 to 70
amonium hydroxide	to pH 5 - 11
amino silane	3 to 25
water	balance

25 The addition of a base to the size is primarily
 for pH control. The amount of base employed is
 sufficient to impart to the size a pH of 3 or higher.
 However, the quantity of base may be increased to impart
 to the size a pH within the size from about 5 to about
 30 11.

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The classical additives of the sizing art may be added to the formulation when necessary like:

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- antioxydant
- processing aids
- humidity regulator
- surfactants to help PU dispersion
- dispersion stabilizer
- antistatic
- lubricants
- stabilizers
- optical brightener
- discolorant
- etc...

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The lubricant may be any normally liquid or solid lubricating material suitable for the purpose. Such materials include vegetable and mineral oils, waxes or various types and certain materials which also have utility as surfactants, such as fatty acid monoesters of polyalkylenegylcols.

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Surfactants that aid dispersion are ethoxylated fatty acids or di-acids, an ethoxylated nonylphenol, and an ethoxylated octylphenol.

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Polyvinyl pyrrolidone (PVP) also may be present for better processing, i.e., strand integrity, size stability and fuzz reduction.

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EXAMPLE I

Our preferred size composition has the
5 following formation:

	parts per 100 <u>parts of solids</u>
polyurethane/isocyanate emulsion; Baxenden 199-76X	26
10 partial amonium salt of acrylic acid, DP-6195 from Allied Colloids	65.6
gamma-aminopropyl triethoxysilane, Union Carbide A-1100	3.4
15 luviskol PVP K90 from BASF 20% solution	5.0
water	balance

The size is efficient on glass fibers from 0.1
to 1.2 LOI.

The aqueous solution has a solids content of
20 6.3 weight percent and a pH of 5-5.5. The size was
applied to individual glass fibers by conventional
application methods and at rates such that the strand
solids, on drying, amounted to about .8% weight percent.

Glass fibers comprising standard length chopped
25 glass fibers having an average length of about 0.125
inches and from about 0.00035-.00039 inch fiber diameter
were produced from the strands.

The present formulation allows for excellent
processability of the sized fibers, i.e., we observed
30 excellent strand integrity, size stability and fuzz

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reduction over standard products for reinforcing nylon resins.

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EXAMPLE II

Sized chopped glass fibers of Example I were compared to standard products. We tested reinforcements from Example I and standard products under hydrolysis pressure at 120°C. We carried out the tests in a medium of 50/50 water/ethylene glycol mixture. Mechanical properties such as tensile strength, tensile elongation, tensile modulus, charpy unnotched impact strength for the products of Example I were essentially the same as for the standard products.

INDUSTRIAL APPLICABILITY

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The sized glass fibers of the invention can be incorporated into the curable matrix resin which is to be reinforced thereby in the final cured resinous article as either monofilament or multi-filament strand, as either long, essentially continuous, elements or short chopped pieces, depending upon the shape and method of fabrication of the article to be formed. The sized glass fibers of this invention are particularly adapted for use in the form of chopped glass fibers. Principal among such reinforcements are glass fibers which generally have diameters of about 0.0025 to 0.0075 inch and lengths of about 0.13 to about 2.00 inch.

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CLAIMS

1. An aqueous size composition consisting
5 essentially of:
a polyurethane/isocyanate emulsion containing
blocked isocyanates;
a homopolymer of acrylic acid monomer;
one or more amino organo-silane coupling
10 agents; and
water.
2. The size composition of claim 1, wherein
the polyurethane/isocyanate dispersion comprises an
aliphatic polyurethane emulsion containing blocked
isocyanate.
- 15 3. The size composition of claim 1, wherein
the polyurethane/isocyanate dispersion comprises an
aqueous emulsion of blocked or unblocked polyurethane
resins comprising an aqueous solution of polyurethane
polymer formed by a reaction between and organic
isocyanate or polyisocyanate and an organic
20 polyhydroxylated compound or hydroxyl terminated
polyether or polyester polymer.
4. The size composition of claim 1, wherein
the polyurethane/isocyanate dispersion comprises an
anionic aliphatic low branched polyester based
25 polyurethane emulsion containing caprolactam blocked
isocyanate having a milky white appearance having a
percent solids of 60, an anionic particle charge, a pH at
25°C of 8.0, and a viscosity of 25°C Brookfield RVT of
150 cps.

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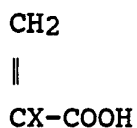
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5. The size composition of claim 1, wherein the polyurethane/isocyanate dispersion comprises an aqueous dispersion of a high molecular weight branched polyurethane polymer based on polyester polyol and 1,1-methylenebis(isocyanatocyclohexane) wherein some of the polymer chains are terminated with blocked isocyanate groups.

6. The size composition of claim 1, wherein the polyurethane/isocyanate dispersion comprises an emulsion of an aliphatic polyurethane containing blocked isocyanate having a milky white appearance, a percent solids of 40, a pH at 25°C of approximately 8-9, and a viscosity at 25°C Brookfield RVT of approximately 200-250 cps.

7. The size composition of claim 1, wherein the polyurethane/isocyanate dispersion comprises a polyurethane and a trimer of 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate blocked with butanone oxime.

8. The size composition of claim 1, wherein the acrylic acid monomer has the formula:



wherein X is a hydrogen atom or a methyl or an alkyl group having 1 to 10 carbon atoms.

9. The size of claim 1 including polyvinyl pyrrolidone.

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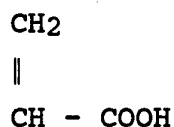
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10. The size composition of claim 1, wherein acrylic acid polymer has molecular weight in the range of about 750 to about 10×10^6 .

11. The size composition of claim 10, wherein the molecular weight ranges from 2000 to 75,000.

12. The size composition of claim 10, wherein the molecular weight ranges from 2000 to 5000.

13. The size of claim 1, wherein the acrylic acid monomer has the formula:



14. The size composition of claim 1, wherein the acrylic acid polymer is an alkalimetal salt or an ammonium salt.

15. The size of claim 1, wherein the acrylic acid polymer is a salt of any primary, secondary or tertiary amine.

16. The size of claim 1, wherein the acrylic acid polymer is a salt of ammonium hydroxide.

17. The size of claim 1, wherein the amino silane is gamma-aminopropyltriethoxysilane.

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18. The size composition of claim 1 having the following composition:

5		parts per 100 <u>parts of solids</u>
	polyurethane/isocyanate emulsion	5 to 80
	homopolymer of	20 to 90
10	acrylic acid	
	amonium hydroxide	to pH 3 or higher
	amino silane	5 to 50
	water	balance

19. The size of claim 18 including polyvinyl pyrrolidone.

20. The size of claim 1 having the following composition:

		parts per 100 <u>parts of solids</u>
	polyurethane/isocyanate emulsion	20 to 60
20	homopolymer of	30 to 70
	acrylic acid	
	amonium hydroxide	to pH 3 or higher
	amino silane	5 to 25
	water	balance

21. The size of claim 20 including polyvinyl pyrrolidone.

22. Glass fibers sized with aqueous size composition of claim 1.

23. Thermoplastic resins reinforced with the glass fibers of claim 22.

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24. Polyamide resins reinforced with the glass
fibers of claim 22.

5 25. Nylon resins reinforced with the glass
fibers of claim 22.

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INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/US 93/06227

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C03C25/02 C08J5/08 C09D175/04

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)

IPC 5 C03C C08J C09D C08G

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,33 36 845 (BAYER AG) 25 April 1985 see the whole document ---	1,2,17, 22-25
A	US,A,3 814 592 (D.E. MCWILLIAMS ET AL.) 4 June 1974 see the whole document ---	1-6,17, 22-25
A	US,A,3 919 145 (P.S. ECKHOFF) 11 November 1975 see abstract -----	1

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. nal Application No

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