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(54) Title: LIQUID CURABLE RESIN COMPOSITION FOR FAT FIBRE

(57) Abstract

Use of a liquid curable resin composition comprising: (A) 100 parts by weight of radiation curable urethane oligomer comprising a backbone oligomer, urethane linking groups, and a radiation curable terminal group, and having a weight average molecular weight of less than 20,000 and (B) 0.1–10 parts by weight of a polymerization initiator, the resin composition having a viscosity of 8,000–300,000 CPS at 25 °C. The composition exhibits excellent coating shape stability while drawn at a high speed.

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LIQUID CURABLE RESIN COMPOSITION FOR FAT FIBRE

DESCRIPTION OF BACKGROUND ART

Field of the Invention:

The present invention relates to a liquid curable resin composition for the preparation of fat fibre, exhibiting superior shape stability when coated, and more particular, to a liquid curable resin composition which is suitable for use as a coating material for optical fibers and optical fiber ribbons.

Description of related art:

In the production of optical fiber, a resin coating is provided for protection and reinforcement after spinning molten glass fiber. This step is called a drawing step. A known structure of the resin coating consists of a primary coating layer of a flexible resin which is coated on the surface of optical fiber, a secondary coating layer of a rigid resin which is provided over the primary coating layer, and a protective coating layer of a thick resin provided outside the secondary coating layer. The resin composition for forming the primary coating is called a soft material; the resin composition for forming the secondary coating is called a hard material. In certain applications it is necessary to apply another coating to increase the thickness of a coated optical fiber with only the soft and the hard layer, as this yields a fiber with a thickness of 200-280 μm. The fiber with increased thickness has an outer diameter in excess of 500 μm, and may be denoted as "fat fibre". The resin composition for producing the external thick coating layer is called an up-jacket material.

An object of the present invention is to provide a liquid curable resin composition which exhibits minimal deformation due to dripping of liquid when the composition is coated by drawing at a high speed, and is suitable as a coating material for optical fiber, particularly as an up-jacket material.

SUMMARY OF THE INVENTION

These objects of the present invention can be achieved by the use of a liquid curable resin composition comprising (A) 100 parts by weight of radiation curable urethane oligomer comprising a backbone oligomer, urethane linking groups, and a radiation curable terminal group, and having a weight average molecular weight of less than 20,000 and (B) 0.1-10 parts by weight of a polymerization initiator, the resulting resin having a viscosity of 8,000-300,000 CPS at 25°C.

Other objects, features and advantages of the invention will hereinafter become more readily apparent from the following description.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENT

The radiation curable urethane oligomer (A) used in the present invention can be prepared by reacting (a) backbone oligomer having hydroxyl groups, further also denoted as a polyol, (b) a diisocyanate, and (c) a compound having a radiation curable group and having a hydroxyl group, e.g. a (meth)acrylate having a hydroxyl group, specifically, by reacting the isocyanate group of the diisocyanate with each of the hydroxyl groups of the polyol and of the compound having a radiation curable group (c).

The radiation curable, liquid resin

composition is advantageously used in a process to make thick coated optical fibers. Hence, the invention also pertains to a method for making coated optical fibers with a total diameter in excess of 500 μm that comprises the following steps:

a) coating a freshly drawn optical fiber of a diameter of about 100-160 μm with a primary, soft, coating and a secondary hard coating to obtain a coated optical fibre with a diameter of 200-280 μm and

b) applying on said coated optical fiber in a thickness sufficient to provide a coated fiber with a total diameter in excess of about 500 μm of a radiation curable coating composition comprising (A) 100 parts by weight of radiation curable urethane oligomer comprising a backbone oligomer, urethane linking groups, and a radiation curable terminal group, and having a weight average molecular weight of less than 20,000 and (B) 0.1-10 parts by weight of a polymerization initiator, the resulting resin having a viscosity of 8,000-300,000 CPS at 25°C, and

c) curing said coating.

In this process, step a) is conventional in the art, and this step needs no further detail for the man skilled in the art. For step b) thick coatings had been applied which were thermoplastic extruded coatings. This had the disadvantage of being a slow process. The use of UV curable coatings permitted speeding up the process, but had the disadvantage of showing irregularities and dripping before curing took place. Now, according to the invention the viscosity of the liquid curable resin composition of the present invention is normally in the range of about 8,000 to about 300,000 CPS at 25°C, and preferably about 10,000 to about 300,000 CPS at 25°C, and most preferably, about 14,000 to about 300,000 CPS. Deformation at the

time of application tends to occur if the viscosity is outside the range of about 8,000 to about 300,000 CPS. Furthermore, the thick coating has outstanding properties as to flexibility and toughness. Preferably, the elongation at break is higher than about 10%, more in particular higher than about 30%. The tensile modulus preferably is higher than about 5 MPa, more preferably higher than about 30 MPa.

The radiation curable resin used for the thick coating preferably is formulated such that the cured coating has a water absorption of less than 4 wt.%, and water extractables of less than 4 wt.%. The acetone extractables should preferably be less than 10 wt.% and the gasoline swelling less than 50 wt.%, all measured on a 150 μm thick, cured coating.

The diameter of the thick fiber preferably is such that the final diameter of the fiber is less than about 1000 μm, hence the thick coating has a thickness of about 100 μm or higher and about 500 μm or less.

The reaction for the preparation of the radiation curable urethane oligomer can be carried out, for example, by the following methods: a method of simultaneously reacting the polyol, the diisocyanate, and the (meth)acrylate having a hydroxyl group; a method of reacting the polyol and the diiscocyanate to obtain an intermediate compound, and reacting this intermediate compound with the (meth)acrylate having a hydroxyl group; a method of reacting the (meth)acrylate having a hydroxyl group and the diisocyanate, and then reacting the resulting compound with the polyol; a method of reacting the (meth)acrylate having a hydroxyl group and the diisocyanate, reacting the resulting compound with the polyol, then again reacting with the (meth)acrylate having a hydroxyl group.

Examples which can be given of the polyol (a) used in these reactions include polyether diols, 15polyester diols, polycarbonate diols, and

polycaprolactone diols. These polyols may be used either individually or in combination of two or more. The manner of polymerization of each constitutional unit in these polyols is not specifically limited and may be random polymerization, block polymerization, or graft polymerization. Given as examples of aliphatic polyether diols among these polyols are polyethylene glycol, polypropylene glycol, polytetramethylene glycol, polyhexamethylene glycol, polyheptamethylene glycol, polydecamethylene glycol, and polyether diols obtained by the ring-opening copolymerization of two or more ionic-polymerizable cyclic compounds. Examples of the ionic-polymerizable cyclic compound include cyclic ethers such as ethylene oxide, propylene oxide, butene-1-oxide, isobutene oxide, 3,3'-bischloromethyloxetane, tetrahydrofuran, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, dioxane, trioxane, tetraoxane, cyclohexene oxide, styrene oxide, epichlorohydrine, glycidyl methacrylate, allyl glycidyl ether, allyl glycidyl carbonate, butadiene monoxide, isoprene monoxide, vinyl oxetane, vinyl tetrahydrofuran, vinyl cyclohexene oxide, phenyl glycidyl ether, butyl glycidyl ether, and glycidylbenzoate. Specific examples of the polyether diol obtained by the ring-opening copolymerization of two or more types of these ionic polymerizable cyclic compound include binary copolymers obtained by the combination of tetrahydrofuran and propylene oxide, tetrahydrofuran and 2-methyltetrahydrofuran, tetrahydrofuran and 3-methyltetrahydrofuran, tetrahydrofuran and ethylene oxide, propylene oxide and ethylene oxide, and ethylene oxide and butene-1-oxide; and ternary copolymers obtained by the combination of tetrahydrofuran, ethylene oxide and butene-1-oxide. It is also possible to use a polyether diol obtained by the ring-opening copolymerization of one of the above-mentioned ionic-polymerizable cyclic compounds and a cyclic imine such

as ethylene imine, a cyclic lactone such as β-propiolactone and glycolic acid lactide, or a cyclic siloxane such as dimethylcyclopolysiloxane.

The above-mentioned aliphatic polyether diols are commercial available under the trademarks, for example, of PTMG 650, PTMG 1000, PTMG 2000 (Mitsubishi Chemical); PPG 400, PPG 1000, PPG 2000, PPG 3000, EXCENOL 720, EXCENOL 1020, 2020, (Asahi Oline); PEG 1000, UNISAFE DC 1100, UNISAFE DC 1800 (Nippon Oil and Fats Co., Ltd.); PPTG 2000, PPTG 1000, PTG 400, PTGL 2000 (Hodogaya Chemical Co., Ltd.); and Z-3001-U, Z-3001-5, PBG 2000A, PBG 2000B (Dai-ichi Kogyo Seiyaku).

Alkylene oxide adducts to hydrogenated bisphenol A, alkylene oxide adducts to hydrogenated bisphenol F, and alkylene oxide adducts to 1,4-cyclohexane diol are given as examples of alicyclic polyether diol.

Alkylene oxide adduct to bisphenol A, alkylene oxide adduct to bisphenol F, alkylene oxide adduct to naphthohydroquinone, and alkylene oxide adduct to anthrahydroquinone are given as examples of aromatic polyether diols. The aromatic polyether diols are also commercially available under the trademarks, for example, of Uniol DA400, DA700, DA1000 and DA4000 (Nippon Oil and Fats Co., Ltd.).

Polyester diols obtained by the reaction of a polyhydric alcohol and a polybasic acid are given as examples of the polyester diol. Ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,6-hexane diol, neopentylene glycol, 1,4-cyclohexane dimethanol, 3-methyl-1,5-pentane diol, 1,9-nonane diol, and 2-methyl-1,8-octane diol, are given as examples of the polyhydric alcohol. As examples of the polybasic acid, phthalic acid, isophthalic acid, terephthalic acid, maleic acid, fumaric acid, adipic acid, and sebacic acid can be given. Commercially

available polyester diols which can be used include, for example, Kurapole P-2010, PMIPA, PKA-A, PKA-A2, PNA-2000 (Kuraray).

A polycarbonate of polytetrahydrofuran and a polycarbonate of 1,6-hexane diol can be given as examples of the polycarbonate. The polycarbonate can also be commercially available under the trademarks, for example, of DN-980, DN-981, DN-982, DN-983 (Nihon Polyurethane), PC-8000 (PPG of the US), and PC-THF-CD (BASF).

Given as examples of the polycaprolactone diols are polycaprolactone diols obtained by the reaction of ε-caprolactone and a diol. Such a diol may be, for example, ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,2-polybutylene glycol, 1,6-hexane diol, neopentyl glycol, 1,4-cyclohexane dimethanol, and 1,4-butane diol. These polycaprolactone diols can be also commercially available under the trademarks such as PLACCEL 205, 205AL, 212, 212AL, 220, 220AL (Daicell Co., Ltd.).

Other polyol compounds which can be used include dimethylol compounds of ethylene glycol, propylene glycol, 1,4-butane diol, 1,5-pentadiol, 1,6-hexane diol, neopentylglycol, 1,4-cyclohexane dimethanol, hydrogenated bisphenol A, hydrogenated bisphenol F, or dihydroxydicyclopentadiene; tricyclodecane dimethanol, pentacyclopentadecane dimethanol, β-methyl-γ-valerolactone, polybutadiene with terminal hydroxyl groups, hydrogenated polybutadiene with terminal hydroxyl groups, castor oil-denatured polyol, polydimethylsiloxane with terminal diols, and polydimethylsiloxane carbitol-denatured polyols.

The number average molecular weight of the polyol (a) is usually 100-15,000, and preferably 500-8,000.

Given as examples of the diisocyanate (b) used in the present invention are 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, tetramethylene-xylylene diisocyanate, 1,5-naphthalene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethylphenylene diisocyanate, 4,4'-biphenylene diisocyanate, 1,6-hexane diisocyanate, isophorone diisocyanate, methylenebis(4-cyclohexylisocyanate), 2,2,4-trimethylhexamethylene diisocyanate, bis(2-isocyanate-ethyl)fumarate, 6-isopropyl-1,3-phenyl diisocyanate, 4-diphenylpropane diisocyanate, lysine diisocyanate, hydrogenated diphenyl methane diisocyanate, and 2,5 (or 6)-bis(isocyanatemethyl)-bicyclo[2.2.1]heptane.

Among these diisocyanates, 2,4-tolylene diisocyanates, isophorone diisocyanates, xylylene diisocyanates, and methylenebis(4-cyclohexylisocyanate) are particularly preferred.

These diisocyanates may be used either individually or in combination of two or more.

The compound having a radiation curable group and having a hydroxy group can comprise e.g. a vinylether, acrylate, methacrylate, vinylester or N-vinyl-group. In particular acrylate or methacrylate are preferred. Examples of suitable compounds are e.g. hydroxy-butyl vinylether or hydroxy-cyclohexyl-vinyl carboxylate.

Examples of the (meth)acrylate having a hydroxyl group (c) used in the present invention include 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 2-hydroxy-3-phenyloxypropyl (meth)acrylate, 1,4-butanediol mono(meth)acrylate, 2-hydroxyalkyl (meth)acryloyl phosphate, 4-hydroxycyclohexyl

(meth)acrylate, 1,6-hexanediol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolethane di(meth)acrylate, pentaerythritol trim(meth)acrylate, dipentaerythritol penta(meth)acrylate, (meth)acrylates represented by the following structural formulas (1) or (2),

$CH_2=C(R^1)-COOCH_2CH_2-(OCOCH_2CH_2CH_2CH_2CH_2)_n-OH$ (1)

$CH_2=C(R^1)-COOCH_2CH_2(OH)CH_2-O-(C_6H_5)$ (2)

wherein R^1 is a hydrogen atom or a methyl group and n denotes an integer of 1-15. In addiiton, compounds obtained by an addition reaction between compounds containing a glycidyl group, such as, alkyl glycidyl ether, allyl glycidyl ether, or glycidyl (meth)acrylate, and (meth)acrylic acid can also be used. Among these (meth)acrylates having a hydroxyl group, particularly desirable are 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate.

These radiation-curable compounds having a hydroxyl group may be used either individually or in combination of two or more.

The polyol (a), the diisocyanate (b), and the (meth)acrylate containing a hydroxyl group (c) are used preferably in a proportion such that for one equivalent of the hydroxyl group of the polyol, 1.1-3 equivalents of the diisocyanate group contained in the diisocyanate compounds and 0.2-1.5 equivalents of the hydroxyl group contained in the (meth)acrylate are used.

Beside the above-mentioned components, a urethane (meth)acrylate produced by the reaction of one mol of diisocyanate and two mols of (meth)acrylate compound having a hydroxyl group may be used for preparing the liquid curable resin composition of the present invention. Given as examples of such urethane (meth)acrylates are the reaction product of hydroxyethyl (meth)acrylate and 2,4-tolylene diisocyanate, the reaction product of hydroxyethyl (meth)acrylate and 2,5 (or 6)-bis(isocyanatemethyl)-

bicyclo[2.2.1]heptane, the reaction product of hydroxyethyl (meth)acrylate and isphorone diisocyanate, the reaction product of hydroxypropyl (meth)acrylate and 2,4-tolylene diisocyanate, and the reaction product of hydroxypropyl (meth)acrylate and isophorone diisocyanate.

In the reaction for preparing the urethane (meth)acrylate (A), a urethanization catalyst such as copper naphthenate, cobalt naphthenate, zinc naphthenate, n-butyl-tin-laurylate, triethylamine, 1,4-diazabicyclo[2.2.2]octane, or 2,6,7-trimethyl-1,4-diazabicyclo[2.2.2]octane is used, generally, in an amount of 0.01 to 1 part by weight for 100 parts by weight of the reaction raw materials. The reaction temperature is normally in the range of 10-90°C, preferably of 30-80°C.

The urethane (meth)acrylate (A) has a weight average molecular weight reduced to polystyrene of less than 20,000, preferably 300-8,000, and more preferably 500-5,000. If the weight average molecular weight is larger than 20,000, the curing speed is retarded so that the productivity of optical fiber is reduced.

The liquid curable resin composition of the present invention is cured by radiation optionally assisted with heat. As the polymerization initiator (B) in the present invention a radiation polymerization initiator can be used optionally in combination with a heat polymerization initiator. Here, the radiation means radiations such as visible light, ultraviolet light, X-rays, electron beams, α-rays, β-rays and γ-rays. Preferably, the radiation is UV and/or visible light.

A heat polymerization initiator such as a peroxide or an azo compound is usually used when the liquid curable resin composition is cured by heat. Given as specific examples of the heat polymerization initiator are benzoyl peroxide, t-butyloxybenzoate, and

azobisisobutylonitrile.

When the liquid curable resin composition of the present invention is cured with UV or visible radiation, a radiation polymerization initiator is used. Examples of the radiation polymerization initiator include 1-hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-2-phenylacetophenone, xanthone, fluorenone, benzaldehyde, fluorene, anthraquinone, triphenylamine, carbazole, 3-methylacetophenone, 4-chlorobenzophenone, 4,4'-dimethoxybenzophenone, 4,4'-diaminobenzophenone, Michler's ketone, benzoin propyl ether, benzoin ethyl ether, benzyl dimethyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 2-hydroxy-2-methyl-1-phenylpropan-1-one, thioxanthone, diethylthioxanthone, 2-isopropylthioxanthone, 2-chlorothioxanthone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one, 2,4,6-trimethylbenzoyldiphenyl-phosphine oxide, and bis)2,6-dimethoxybenzoyl-2,4,4-trimethylpentylphosphine oxide; and commercially available products, such as Irgacure 184, 369, 651, 500, 907, CGI1700, CGI1750, CGI1850, CG24-61 (Ciba Geigy), Lucirin LR8728 (BASF), Darocure 1116, 1173 (Merck Co.), and Uvecryl P36 (UCB).

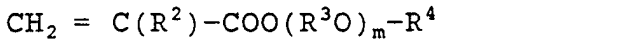
The above-described heat polymerization initiator may be used together with the radiation polymerization initiator when the liquid curable resin composition of the present invention is cured with radiation. The polymerization initiators are used in an amount of 0.1-10 parts by weight, preferably 0.5-7 parts by weight, for 100 parts by weight of the urethane (meth)acrylate (A).

When the liquid curable resin composition of the present invention is cured with radiation, a photo-sensitizer may be used together with the radiation polymerization initiator. Given as examples of the photo-sensitizers are triethylamine, diethylamine, N-dimethyldiethanolamine, ethanolamine, 4-

dimethylaminobenzoate, and commercially available products such as Uvecryl P102, P103, P104 and P105 (manufactured by UCB Co.). These photo-sensitizers are added to the composition in an amount of less than 10 parts by weight.

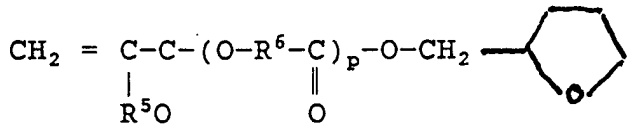
A reaction diluent is used for adjusting the viscosity of the liquid curable resin composition of the present invention. There are monofunctional compounds and polyfunctional compounds in the reaction diluent. Examples of the monofunctional compound N-vinyl pyrrolidone, N-vinyl caprolactam, isobornyl (meth)acrylate, bornyl (meth)acrylate, tricyclodecanyl (meth)acrylate, dicyclopentanyl (meth)acrylate, dicyclopentenyl (meth)acrylate, cyclohexyl (meth)acrylate, benzyl (meth)acrylate, 4-butylcyclohexyl (meth)acrylate, acryloyl morpholine, vinyl imidazole, vinyl pyridine, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrfylate, isopropyl (meth)acrylate, butyl (meth)acrylate, amyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, pentyl (meth)acrylate, isoamyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, isooctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, isodecyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, isostearyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, butoxyethyl (meth)acrylate, ethoxydiethylene glycol (meth)acrylate, benzyl (meth)acrylate, phenoxyethyl (meth)acrylate, polyethylene glycol (meth)acrylate, polypropylene glycol mono(meth)acrylate, methoxyethylene glycol (meth)acrylate, ethoxyethyl (meth)acrylate, methoxypolyethylene glycol (meth)acrylate,

methoxypolypropylene glycol (meth)acrylate, diacetone (meth)acrylamide, isobutoxymethyl (meth)acrylamide, N,N-dimethyl (meth)acrylamide, t-octyl (meth)acrylamide, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylae, 7-amino-3,7-dimethyloctyl (meth)acrylate, N,N-diethyl (meth)acrylamide, N,N-dimethylaminopropyl (meth)acrylamide, hydroxybutyl vinyl ether, lauryl vinyl ether, cetyl vinyl ether, 2-ethylhexyl vinyl ether; and compounds represented by the following formules (3) to (5).



$$CH_2 = C(R^2)-COO(R^3O)_m-R^4 \qquad (3)$$

wherein R^2 is a hydrogen atom or a methyl group; R^3 is an alkylene group containing 2 to 6, preferably 2 to 4 carbon atoms; R^4 is a hydrogen atom or an alkyl group containing 1 to 12, preferably 1 to 9, carbon atoms; and m is an integer from 0 to 12, and preferably from 1 to 8.



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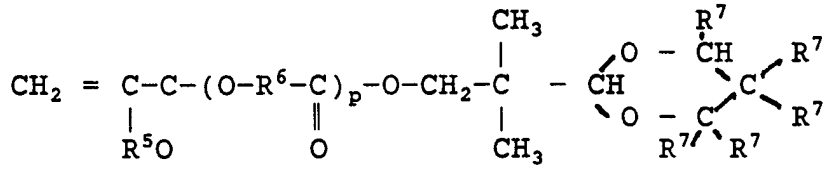

(5)

wherein R^5 is a hydrogen atom or a methyl group; R^6 is an alkylene group containing 2 to 8, preferably 2 to 5, carbon atoms; R^7s are individually a hydrogen atom or a methyl group, and p is an integer from 1 to 4.

Commercially available monofunctional compounds include ARONIX M111, M113, M114, M117

(Toagosei Chemical Industry Co., Ltd.), KAYARAD TC110S, R629, R644 (Nippon Kayaku Co., Ltd.), and Viscoat 3700 (Osaka Organic Chemical Industry Ltd.).

Examples of the polyfunctional compounds as the reaction diluent include trimethylolpropane tri(meth)acrylate, pentaerythritol (meth)acrylate, ethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, trimethylolpropanetrioxyethyl (meth)acrylate, tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate, tris(2-hydroxyethylisocyanurate di(meth)acrylate, tricyclodecanedimethanol di(meth)acrylate, and di(meth)acrylate of a diol which is an ethylene oxide or propylene oxide adduct to bisphenol A, di(meth)acrylate of a diol which is an ethylene oxide or propylene oxide adduct to hydrogenated bisphenol A, di(meth)acrylate of a diol which is an ethylene oxide or propylene oxide adduct to hydrogenated bisphenol A, epoxy (meth)acrylate which is a (meth)acrylate adduct to bisphenol-A-diglycidyl ether, and triethylene glycol divinyl ether tricyclodecandimethanol di(meth)acrylate. Given as commercially available polyfunctional compounds are YUPIMER-UV, SA1002, SA2007 (Mitsubishi Chemical Co., Ltd.), Viscoat 700 (Osaka Organic Chemical Industry Ltd.), KAYARAD R-604, DPCA-20, DPCA-30, DPCA-60, DPCA-120, HX-620, D-310, D-330 (Nippon Kayaku Co., Ltd.), and ARONIX M-210, M-215, M-315, M-325 (Toagosei Chemical Industry Co., Ltd.).

These reaction diluents may be used either individually or in combination of two or more, and are preferably added to the composition in an amount of less than 80 parts by weight, preferably 10-55 parts by weight, for 100 parts by weight of the component (A). If this amount is more than 80 parts, the viscosity of the resulting composition may be small so that the

composition tends to be deformed after coating.

Beside the above-described urethane (meth)acrylate (A), polymerization initiator (B), and reaction diluent, the liquid curable resin composition of the present invention may be formulated with various components, such as other oligomers or polymers and additives, to the extent that the characteristics of the resin composition is not adversely affected.

Included in the examples of the other oligomers are fluorine-type oligomers. As examples of the polymers, epoxy resins, polyamide, polyamide imide, polyurethane, polybutadiene, chloroprene, polyether, polyester, pentadiene derivatives, styrene/butadiene/styrene block copolymers, styrene/ethylene/butene/styrene block copolymers, styrene/isoprene/styrene block copolymers, petroleum resins, xylene resins, and ketone resins are given.

Furthermore, diamines may be added to the liquid curable resin composition of the present invention to supprress generation of hydrogen gas which causes a transmission loss of optical fibers. The diamines which can be added include ethylenediamine, tetramethylenediamine, hexamethylenediamine, para-phenylenediamine, 4,4'-diaminodiphenylmethane, and polyether diamine. These diamines may be added at a proportion of less than 1 part by weight to the composition.

Beside these components, various additives may be added as required, such as antioxidants, coloring matters, UV absorbers, photo-stabilizes, silane coupling agents, thermal polymerization inhibitors, leveling agents, surface active agents, preservatives, plasticizers, lubricants, solvents, fillers, aging preventives, wettability improvers, and coated surface improvers. In particular coloring materials are useful additives as this allows individual fibers to be recognised, if they are used in

a bundle of fibers. Coloring materials preferably are used in an amount of 0.5-10 wt.%, and have an average particle size preferably of less than 20 μm, more preferably less than 5 μm and more in particular less than 3 μm.

The present invention will be hereinafter described in more detail by way of examples which are given for illustration of the present invention shall not to be construed as limiting the present invention. In the examples hereinafter "part(s) by weight" is simply described as "part(s)".

Examples

Synthetic Example 1

32.9 parts of 2,4-tolylene diisocyanate, 0.02 part of 2,6-di-tert-butyl-p-cresol, 0.01 part of phenothiadine, and 0.09 part of dibutyl tin dilaurate were charged to a reaction vessel equipped with a stirrer. The mixture was cooled with ice to 10°C or lower while stirring. After adding 31.2 parts of hydroxyethyl acrylate dropwise while controlling the temperature below 20°C, the mixture was reacted for a further one hour while stirring. Then, 35.7 parts of polytetramethylene glycol having a number average molecular weight of 650 was added and the mixture was stirred for 5 hours at 50-60°C. The reaction was terminated when the residual isocyanate was reduced to 0.1 wt.%. The urethane acrylate obtained is designated as HU-1.

Synthetic Example 2

32.4 parts of 2,4-tolylene diisocyanate, 0.02 part of 2,6-di-tert-butyl-p-cresol, 0.01 part of phenothiadine, and 0.192 part of dibutyl tin dilaurate were charged to a reaction vessel equipped with a stirrer. The mixture was cooled with ice to 10°C or

lower while stirring. After adding 30.8 parts of hydroxyethylene acrylate dropwise while controlling the temperature below 20°C, the mixture was reacted for a further one hour while stirring. Then, 36.6 parts of polypropylene diol having a number average molecular weight of 700 was added and the mixture was stirred for 10 hours at 50-60°C. The reaction was terminated when the residual isocyanate was reduced to 0.1 wt.%. The urethane acrylate obtained is designated as HU-2.

Synthetic Example 3

32.0 parts of 2,4-tolylene diisocyanate, 0.03 part of 2,6-di-tert-butyl-p-cresol, 0.004 part of phenothiadine, and 0.11 part of dibutyl tin dilaurate were charged to a reaction vessel equipped with a stirrer. The mixture was cooled with ice to 10°C or lower while stirring. After adding 21.4 parts of hydroxyethyl acrylate dropwise while controlling temperature below 20°C, the mixture was reacted for a further one hour while stirring. Then, 30.6 parts of polypropylene diol having a number average molecular weight of 400 and 15.9 parts of polypropylene diol having a number average molecular weight of 1,000 were added and the mixture was stirred for 10 hours at 50-60°C. The reaction was terminated when the residual isocyanate was reduced to lower than 0.1 wt.%. The urethane acrylate obtained is designated as HU-3.

Example 1

100 parts of urethane acrylate HU-1, 15.6 parts of isobornyl acrylate as a reactive diluent, 3.5 parts of 1-hydroxycyclohexyl phenyl ketone as a photo-polymerization initiator, and 0.35 part of 2,2'-thio-diethylenebis[3-(3,5-di-t-butyl-4-hydroxyphenyl)proprionate] as an aging perventive were charged in a vessel with a stirrer and stirred at 50-60°C to obtain the composition of the present

invention.

Example 2

100 parts of urethane acrylate HU-2, 15.6 parts of isobornyl acrylate as a reaction diluent, 3.5 parts of 1-hydroxycyclohexyl phenyl ketone as a photo-polymerization initiator, and 0.35 part of 2,2'-thio-diethylenebis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] as an aging perventive were charged in a vessel with a stirrer and stirred at 50-60°C to obtain the composition of the present invention.

Example 3

100 parts of urethane acrylate HU-3, 40.8 parts of isobornyl acrylate as a reaction diluent, 4.2 parts of 1-hydroxycyclohexyl phenyl ketone as a photo-polymerization initiator, and 0.42 part of 2,2'-thio-diethylenebis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] as an aging perventive were charged in a vessel with a stirrer and stirred at 50-60°C to obtain the composition of the present invention.

Comparative Example 1

100 parts of urethane acrylate HU-2, 55 parts of isobornyl acrylate as a reaction diluent, 4.7 parts of 1-hydroxycyclohexyl phenyl ketone as a photo-polymerization initiator, and 0.47 part of 2,2'-thio-diethylenebis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] as an aging perventive were charged in a vessel with a stirrer and stirred at 50-60°C to obtain the composition of the present invention.

Reference Example

Resin compositions used for the primary

coating and secondary coating of optical fibers were prepared as follows.

<Preparation of primary coating composition>

6.6 parts of 2,4-tolylene diisocyanate, 0.015 part of 2,6-di-tert-butyl-p-cresol, 0.48 part of dibutyl tin dilaurate, 0.005 part of phenothiadine, and 16.2 parts of isobornyl acrylate were charged to a reaction vessel equipped with a stirrer. The mixture was cooled with ice to 10°C or lower while stirring. After adding 2.9 parts of hydroxyethyl acrylate dropwise while controlling temperature below 20°C, the mixture was reacted for a further one hour while stirring. Then, 50.0 parts of polytetramethylene glycol having a number average molecular weight of 2000 was added and the mixture was stirred for 4 hours at 50-60°C. The reaction was terminated when the residual isocyanate was reduced to 0.1 wt.%. To the reaction mixture were added 10.8 parts of isobornyl acrylate, 4.8 parts of vinyl caprolactam, 5.6 parts of lauryl acrylate, and 0.2 parts of 2,2'-thiodiethylenebis[3-(3,5-di-t-butyl-4-hydroxy-phenyl)propionate], and the mixture was stirred for 30 minutes at 40-50°C. After the addition of 0.1 part of diethyl amine while controlling the temperature at 30-40°C, the mixture was stirred for 30 minutes. Next, 1 part of bis-(2,6-methoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide and 1 part of 2-hydroxy-2-methyl-1-phenylpropan-1-one were added while controlling the temperature at 50-60°C. The mixture was stirred until a primary coating material is obtained as a transparent homogeneous liquid.

<Preparation of secondary coating composition>

17.8 parts of 2,4-tolylene diisocyanate, 0.02 part of 2,6-di-tert-butyl-p-cresol, 0.05 part of dibutyl tin dilaurate, and 15.4 parts of isobornyl

acrylate were charged to a reaction vessel equipped with a stirrer. The mixture was cooled with ice to 10°C or lower while stirring. After adding 16.9 parts of hydroxyethyl acrylate dropwise while controlling temperature below 20°C, the mixture was reacted for a further one hour while stirring. Then, 2.94 parts of tricyclodecane dimethanol and 30.0 parts of polytetramethylene glycol (manufactured by Mitsubishi Chemical Corp.) having a number average molecular weight of 2000 were added and the mixture was stirred for 4 hours at 50-60°C. The reaction was terminated when the residual isocyanate was reduced to 0.1 wt.% or smaller. To the reaction mixture were added 12.8 parts of N-vinylpyrrolidone, 1.86 parts of isobornyl acrylate, and 0.29 part of 2,2'-thiodiethylenebis[3-(3,5-di-t-butyl-4-hydroxy-phenyl)propionate], and the mixture was stirred at 50-60°C. Next, 1 part of bis(2,6-methoxybenzoyl)-2,4,4-trimethyl-pentylphosphine oxide and 1 part of 2-hydroxy-2-methyl-1-phenylpropan-1-one were added while controlling the temperature at 50-60°C. The mixture was stirred until a secondary coating material is obtained as a transparent homogeneous liquid.

Test Example

The viscosity and the mold-shape stability of the compositions prepared in the Example 1-3 and the comparison experiment were evaluated, and the number average molecular weight of the urethane acrylate prepared in the Synthetic Example was measured, according to the following methods.
The results are shown in table 1.

(1) Measurement of viscosity

The viscosity of the liquid curable resin compositions was measured at 25°C using B-Type viscometer manufactured by Tokyo Keiki Co., Ltd.

(2) Measurement of the number average molecular weight

of urethane acrylate

The number average molecular weight reduced to polystyrene was measured by gel permeation method using AS-8020™ manufactured by Tosoh Corp.

(3) Evaluation of molded-shape stability

The primary and secondary coating compositions were applied using an optical fiber drawing machine (manufactured by Yoshida Industries) and cured. The composition of the present invention and the comparative composition were coated as the covering for these primary and secondary coatings.

The following drawing conditions were adopted. The primary and secondary coatings were applied to optical fiber with a diameter of 150 μm so as to make the diameter of 260 μm after the secondary coating and the external diameter of 900 μm after coating of the composition of the present invention or the comparative composition. The drawing speeds of optical fiber of 120 m/min, 300 m/min, and 600 m/min were adopted, respectively. The coated compositions were cured by irradiation of UV light using 3.5 KW UV lamp SMC™ manufactured by ORC Co., Ltd. The molded-shape stability was evaluated by macroscopic observation of fluctuation and uneveness of cured thickness.

TABLE 1

		Example 1	Example 2	Example 3	Comparative Example 1
Viscosity (CPS, @25°C)		14,500	90,000	20,000	6,800
Weight average molecular weight of oligomer		1,700	1,650	1,800	1,650
Molded shape stability (drawing speed)	120 m/min	Acceptable	Acceptable	Acceptable	Acceptable
	300 m/min	Acceptable	Acceptable	Acceptable	Unacceptable
	600 m/min	Acceptable	Acceptable	Acceptable	Unacceptable

As can be seen in Table 1, the liquid curable resin composition of the present invention can be drawn at a high speed, while exhibiting excellent coating shape stability.

C L A I M S

1. Use of a liquid curable resin composition comprising:
(A) 100 parts by weight of radiation curable urethane oligomer comprising a backbone oligomer, urethane linking groups, and a radiation curable terminal group, and having a weight average molecular weight of less than 20,000 and
(B) 0.1-10 parts by weight of a polymerization initiator, the resin composition having a viscosity of about 8,000-300,000 CPS at 25°C, as upjacketing material in the manufacture of thick coated optical fibers.

2. The use as claimed in claim 1, in which the composition further comprising less than 55 parts by weight of at least one reactive diluent.

3. The use as claimed in claim 1, wherein the number average molecular weight of the urethane oligomer is 400-5,000.

4. The use as claimed in claim 1, wherein the liquid radiation curable resin composition has a viscosity of about 10,000-300,000 CPS at 25°C.

5. Process for the manufacture of a coated optical fiber with a thickness in excess over 500 μm that comprises the following steps:
a) coating a freshly drawn optical fiber of a diameter of about 100-160 μm with a primary, soft, coating and a secondary, hard, coating to obtain a coated optical fibre with a diameter of 200-280 μm and
b) applying on said coated optical fiber in a thickness sufficient to provide a coated fiber with a total diameter in exess of about 500 μm of a radiation curable coating composition comprising (A) 100 parts by weight of radiation curable urethane oligomer

comprising a backbone oligomer, urethane linking groups, and a radiation curable terminal group, and having a weight average molecular weight of less than 20,000 and (B) 0.1-10 parts by weight of a polymerization initiator, the coating composition having a viscosity of about 8,000-300,000 CPS at 25°C, and

c) curing said coating.

6. Coated optical fiber having a least three coating layers, the outermost coating layer having a thickness of about 100 μm or higher and about 500 μm or less and being a cured coating obtained by radiation cure of a liquid curable resin as described in claim 1, the cured coating has an elongation at break of higher than about 10%.

7. Coated optical fiber according to claim 6, wherein the outermost coating has a tensile modulus of higher than about 5 MPa.

8. Coated optical fiber according to claim 6, wherein the outermost coating has a water absorption of less than 4 wt.%, and water extractables of less than 4 wt.%.

9. Coated optical fiber according to claim 6, wherein the outermost coating has acetone extractables of less than 10 wt.%.

10. Coated optical fiber according to claim 6, wherein the outermost coating has gasoline swelling of less than 50 wt.%.

11. Coated optical fiber according to claim 6, wherein the outermost coating has been provided with a color.

INTERNATIONAL SEARCH REPORT

Interi. nal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C25/02 G02B6/44

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 6 C03C G02B

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

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X	EP 0 141 330 A (DESOTO INC) 15 May 1985 see example 4 ---	1-3,5,6
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Shade, M

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