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(54) Title: METHOD FOR CURING OPTICAL FIBER COATINGS AND INKS BY LOW POWER ELECTRON BEAM RADIATION

(57) Abstract

The present invention relates to a method for making optical fiber coatings, inks and matrix material structures such as bundles or ribbons, using low power electron beam radiation. The optical fiber substrate is not substantially degraded following exposure to the low power electron beam radiation during the curing process.

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METHOD FOR CURING OPTICAL FIBER COATINGS AND INKS BY LOW POWER ELECTRON BEAM RADIATION

BACKGROUND OF THE INVENTION

1. Field of the Invention.

The present invention relates to a method for curing optical glass or thermoplastic fiber coatings and inks, and in particular, for curing pigmented coatings and inks using low power electron beam radiation.

2. Background Information.

Glass or thermoplastic optical fibers are normally coated with an inner primary coating (or "primary coating") and an outer primary coating (or "secondary coating") to protect the properties of the fiber. Coated fiber can be further coated with ink layers to aid in fiber identification. Alternatively, the outer primary coating can be colored to aid in fiber identification. Additional radiation-curable coating compositions, referred to as matrix materials, can be applied to a group of coated optical fibers and then cured to form a protective anchoring structure containing bundles or ribbons of optical fibers. Individual fiber identification can be important when multiple fibers are placed in ribbon or cable structures.

unpigmented coatings can be advantageously subjected to electron beam cure. However, electron beam radiation can damage an underlying glass fiber substrate by ionizing metal atoms in the glass which generates colored centers and increases attenuation of the signal transmitted therein. Electron beams can also damage the resin and adversely affect the coating's mechanical properties. Hence, this method can also have significant disadvantages.

The art has seemingly not yet provided a method of electron beam curing optical fiber coatings, and in particular colored coatings and ink layers, which does not result in damage to the underlying fiber substrate.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a method of electron beam curing optical fiber coatings and inks without substantial fiber damage. It is a further object of the present invention to provide a coated optical glass or thermoplastic fiber which comprises at least one layer which has been cured by electron beam treatment which leaves the underlying fiber substrate substantially unaffected. These objectives are achieved by applying a radiation-curable coating or ink layer to an optical fiber and exposing the layer to electron beam radiation which is produced with an effectively low amount of accelerating voltage to avoid

substantial degradation to the glass or thermoplastic fiber.

The method of this invention can also be used to cure radiation-curable compositions which are used as matrix materials to form bundles or ribbons of coated optical fibers.

As used herein, the term "low power electron beam radiation" means an electron beam produced with an accelerating voltage (i.e., beam power or energy) of about 125 kV or less. In one embodiment, the energy of the beam is about 80 kV or less. In another embodiment of the invention, the energy is about 60 kV or less.

Preferably, the power of the electron beam is adjusted so that the electrons leave the substrate substantially unaffected. The phrase "avoid substantial degradation" means that the appearance (e.g., color) and material properties of the glass substrate are substantially unchanged. The energy is preferably at least about 10 kV, and more preferably, at least about 20 kV, and more preferably, at least about 30 kV.

DETAILED DESCRIPTION OF THE INVENTION

The method of the present invention provides numerous advantages over prior methods of curing optical glass fiber coatings and inks. Because of the penetrating ability of the electron beam, resins comprising high concentrations of pigments can be effectively cured. If so desired, the method can be practiced without

photoinitiators being present in the radiation-curable compositions, thus reducing the cost as well as improving the photooxidative stability of the cured coating. In addition to being less expensive than coatings with initiators, coatings without initiators have less extractables and therefore may be considered for use in direct contact with food in food packaging.

At the same time, however, because the energy of the beam can be controlled, thin layers of resins or inks can be cured without substantial damage to the underlying substrate. In a further advantage over high-energy methods, the present low energy method can result in lower emission of stray radiation during application of the electron beam.

Furthermore, the method of the invention can be used to cure coatings and inks on optical fibers made of thermosetting polymers. Optical fibers of thermosetting polymers are preferably coated with materials which have a refractive index complementary to the thermosetting core of the fiber, such that minimal loss of light occurs during transmission through the coated fibers. As with glass optical fibers, the curing process preferably does not adversely affect the underlying thermoplastic fibers. Thermoplastic optical fibers are disclosed in, for example, U.S. No. 5,292,459, the entire contents of which is incorporated herein by reference.

The method can be practiced using electron beams with an energy of less than about 125 kV. The

energy of the beam can be adjusted depending on the density of the coating, the thickness of the coating, the desired depth of curing, and other factors. For example, a beam of 50-60 kV is normally sufficient to cure to a depth of about 25 mm.

Although the dosage can be varied according to the need, dosages of up to about 30 Mrads can be used. Dosage of about 2-8 Mrads can be effective.

Typically, production of electron beam radiation requires a power source supply and an electron-beam accelerator (i.e., an electron beam apparatus). Preferably the electron beam apparatus comprises one or more electron beam tubes. An example of such an electron beam array is described in Wakalopulos (U.S. Patent No. 5,414,267), incorporated herein by reference. Briefly, Wakalopulos describes a system comprising an array of thin low-Z film (e.g., atomic number less than 20) window electron beam tubes mounted on a support plate. Preferably, the window through which the electrons pass is electron permeable and gas impermeable. In a preferred embodiment, the window comprises silicon carbide, silicon nitride, boron nitride or doped silicon.

Each beam tube generates a stripe-like electron beam which spans part of the width of material being treated at a relatively low voltage. The remainder of the width is treated with stripe-like beams from other tubes, the arrangement of tubes having beams spanning the entire width of material to be cured. The geometric arrangement of the tubes can be varied widely to

accommodate the cylindrical shape of the optical fiber. For example, the tubes may be arrayed at angles (e.g., 120°) from one another to cure coatings and inks on optical fibers in a single pass. Similarly, two or more tubes may be arrayed opposing one another (e.g., 180°) to facilitate the curing of matrix material compositions used to form bundles or ribbons which anchor coated optical fibers.

The apparatus can further contain more than one set of tubes, each set delivering a different dose or intensity of electrons. For example, where it is desirable to reduce inerting, one set of tubes can be set to deliver a high surface dose at a lower voltage to effectively cure the surface of the material. A second set of tubes would be set to deliver a lower dose of higher voltage in order to achieve through cure.

The apparatus can comprise a mechanism for passing the optical fiber beneath the electron beam source in a continuous manner such as a conveyor belt or roller. When curing matrix material coating compositions used to form bundles, ribbons or cables, opposing tubes may be positioned above and below the material being cured. The curing rate is rapid (e.g., less than 1 second), and can be effectively achieved in a single pass. While the distance between the beam and the material may be varied according to need, it has been found that a distance of about 0.5cm to about 2cm, measured from the surface of the electron beam tube window to the surface of the coating, is effective.

The method can be applied to coated fibers having multiple coating layers including fibers which comprise an ink layer. The optical fiber coatings may be cured via a wet-on-wet process whereby the inner primary and outer primary coatings are applied wet and cured in one step. Alternatively, the coatings may be cured using a wet-on-dry process whereby the first coat is cured prior to application of the second coat. Optical fiber coatings and processes for coating fiber are disclosed in, for example, U.S. Patent No. 4,099,837 or its Reissue Patent No. 33,677 and U.S. Patent No. 5,104,433, which are hereby incorporated by reference. U.S. Patent No. 5,336,563 also discloses suitable optical fiber primary coatings which is hereby incorporated by reference. U.S. Patent No. 5,456,984 discloses matrix material compositions which can be used to form bundles or ribbons suitable for anchoring coated optical fibers, which is hereby incorporated by reference. Fibers also can be sprayed electrostatically and passed beneath the source in an inert atmosphere.

Single or multi-mode fiber can be used.

The coated optical fiber can comprise an outer primary layer (secondary layer) which is tough or hard enough to protect the optical fiber and any underlying coatings. The underlying coatings can be inner primary coatings which are typically softer in comparison to the outer primary layer. These individual layers, including the outer primary layer, can be cured by any methods known in the art, or may be cured using the

methods of the present invention.

Coated optical fibers can be bundled together using radiation-curable matrix materials in ribbon structures which typically comprise 2 to 12 fibers. Ribbon structures can be bundled in multiple layers and/or configurations depending upon the ultimate application or use of the bundled fibers. These matrix materials can be cured by any methods known in the art, or may be cured using the methods of the present invention. The coated optical fibers can be colored to differentiate the fibers. To allow for easy access to these individual fibers, the coating composition may comprise a release agent. Suitable release agents include silicones, silicone acrylates, fluoro-carbon oils or resins and the like. Where such agents are used, the optical fiber coatings preferably comprise 0.5-20 wt. % of a suitable release agent.

Although the present methods may be widely applied to a variety of polymer systems, typically the methods of the present invention will be used to cure polymer coatings and inks amenable to cure by UV radiation but in general, no UV-sensitive photoinitiator is needed. UV curable polymers are those which undergo free-radical polymerization, generally with the aid of a photoinitiator. Electrons act as an external catalyst used when needed to apply to materials responsive to free radical polymerization or free radical generation through chemical bond breaking and re-combination within a polymer chain structure or between polymer chains to form

a cross link. The reactions occurring on exposure to electron radiation include initiation reactions; propagation reactions; and termination reactions. In addition, the various types of reactions may result in crosslinking as well as chain scission.

The invention may be used to cure ink coating compositions for coating and identifying optical glass or thermoplastic fibers. Curable ink coatings are usually about 3 to about 10 microns thick, and tend to be concentric to prevent attenuation of signal transmission through the fiber. Such ink coatings typically have a T_g of at least about 30°C, and more preferably of at least about 50°C. Compositions for ink coatings can be tailored to optimize desirable properties, often by reformulating compositions initially designed as outer primary coatings, and including desired additives.

Radiation-curable coatings and vehicles for radiation-curable inks are well known in the art, and ingredients are usually selected from acrylate or methacrylate functional oligomers, monofunctional or polyfunctional acrylate diluents, photoinitiators, stabilizers, pigments, and waxes. The oligomers most commonly used are the acrylate and methacrylate derivatives of saturated polyesters, aromatic, aliphatic, and cycloaliphatic epoxy resins, aromatic and aliphatic polyurethanes and polyether polyols. Thiol-ene and thiol-amide systems, wherein polymerization occurs between a group possessing allylic unsaturation and a group containing a tertiary amine or thiol are also suitable.

Film properties such as toughness, adhesion, gloss and flexibility may be varied depending on the oligomer(s) used.

The coating and ink compositions may further comprise one or more diluents. Reactive diluents are monomers used primarily to adjust the viscosity of these systems and control cure speed and cross-link density. Monomers or mixtures of monomers having an acrylate or vinyl ether functionality and an C_4-C_{20} alkyl or polyether moiety may be used. Compounds having an aromatic group may also be included as reactive diluents. Suitable diluents include pentaerythritol, tri- and tetraacrylate, tripropylene glycol diacrylate, trimethylolpropane triacrylate and their alkoxylated derivatives.

Additional suitable reactive diluents include hexylacrylate, 2-ethylhexylacrylate, isobornylacrylate, decylacrylate, laurylacrylate, stearylacrylate, 2-ethoxy-ethylacrylate, laurylvinylether, 2-ethylhexylvinylether, n-vinyl formamide, isodecyl acrylate, vinyl-caprolactam, isooctylacrylate, n-vinylpyrrolidone, and the like. Diluents with aromatic groups include ethylene glycolphenylether-acrylate, polyethylene glycolphenyl-ether-acrylate, polypropylene glycolphenylether-acrylate and alkyl-substituted phenyl derivatives of these compounds.

If the functional group of the oligomer or monomer comprises a thiol-ene or an amine-ene system, reactive diluents having allylic unsaturation may be used, such as diallylphthalate, triallyltri-mellitate,

triallylcyanurate, triallylisocyanurate and diallylisophthalate. For amine-ene systems, amine functional diluents, including adducts of, for example, trimethylolpropane, isophorone diisocyanate and di(m)ethylethanolamine, or the adduct of hexanediol, isophorone diisocyanate and dipropylethanolamine may be used.

The present method may be used to cure ink coating compositions without the need of a photoinitiator. Optionally the ink or coating composition may comprise one or more photoinitiators, typically present in an amount between about 0.1 and 10 weight percent. Cationic initiators, such as triarylsulfonium salts, alkylarylsulfonium salts, diaryliodonium salts, diarylchloronium and diarylbromonium salts arylammonium, arylphosphonium and arylarsonium salts and triphenylselenonium salts are suitable. In particular, mixed triarylsulfonium hexafluoroantimonate salts and mixed triarylsulfonium hexafluorophosphate salts are suitable.

Examples of free radical-type photoinitiators include hydroxycyclohexylphenyl ketone; hydroxymethyl-phenylpropanone; dimethoxyphenylacetophenone; 2-methyl-1-[4-(methyl thio)-phenyl]-2-morpholinopropanone-1; 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one; 1-(4-dodecyl-phenyl)-2-hydroxy-2-methylpropan-1-one; 4-(2-hydroxyethoxy)phenyl-2(2-hydroxy-2-propyl)-ketone; diethoxyphenyl acetophenone; 2,4,6 trimethylbenzoyl diphenylphosphone, a mixture of (2,6-dimethoxy benzoyl)-

2,4,4 trimethylpentylphosphineoxide and 2-hydroxy-2-methyl-1-phenyl-propane-1-one, and mixtures thereof.

In addition to the acrylate-functional diluents and oligomers used in UV radiation systems, methacrylates, maleics and certain allyl functional oligomers and diluents can be readily copolymerized by electron beam without photoinitiators due to the presence of the energized electrons.

The use of pigments in coatings and inks is well known in the art, as well as methods of their application. Either a colorant is added to the outer primary coating or an ink coating is formed on the outer primary coating of the optical glass fiber to obtain a color-coated optical fiber. Ink compositions and colorants added to the outer primary coatings are now well known in the art. Examples of suitable ink compositions, include, for example, those described in published European application number 0614099A2 and U.S. Patent Nos. 4,900,126 and 4,953,945, the complete disclosure of which are incorporated herein by reference.

The method of the present invention can be used to cure coating and ink compositions which contain any combination of organic and/or inorganic pigments known in the art. Pigments normally do not play a significant role during radiation curing as they are relatively inert towards electron beams. However, they may have an indirect influence as they have a substantial effect on the density of the compound which, in turn, affects the penetration depth of the electron beams.

Therefore, the energy of the electron beam may need to be varied according to the properties of the particular pigments used as well as composition density. Also, the composition which is cured by electron beam radiation preferably does not have a thickness which substantially exceeds the mean free path of electrons in the cured media.

Suitable inorganic pigments include, for example, titanium dioxide, zinc oxide, zinc sulfide, barium sulfate, aluminum silicate, calcium silicate, carbon black, black iron oxide, copper chromite black, iron oxides, chromium oxide greens, iron blue, chrome green, violet (e.g., manganese violet, cobalt phosphate, $CoLiPO_4$), lead chromates, lead molybdates; and cadmium, titanate, pearlescent and metallic pigments.

Suitable organic pigments include, for example, monoazo pigments, di-azo pigments, di-azo condensation pigments, quinacridone pigments, dioxazine violet, vat pigments, perylene pigments, thioindigo pigments, phthalocyanine pigments and tetrachloroisoindoliniones.

The coating and ink composition to be cured may further comprise other materials well known in the polymer art, such as stabilizers, adhesion-promoters, light sensitive and light absorbing components, catalysts, initiators, lubricants, wetting agents, antioxidants, dispersing agents and the like.

The method of the invention may be used to cure matrix-forming coating compositions. Acceptable

matrix-forming compositions comprise at least one oligomer and preferably also a reactive diluent with a reactive functional group capable of undergoing polymerization upon cure. Examples of such functional groups include epoxy groups, thiol-ene or amine-ene systems, and ethylenic unsaturation such as acrylamide, acrylate, methacrylate, vinylether or malate vinylether functionalities. Preferably, the cured matrix material possesses a swell index and T_g that provide for both mid-span access of the coated optical glass fibers using a solvent stripping method, and end-access of the optical glass fibers using a heat stripping method.

The electron-beam curable matrix-forming composition may also contain a diluent having a functional group capable of co-polymerization with the reactive functional group of the oligomer in the composition. Examples of diluents include acrylate monomers, such as isobornylacrylate, hexanediol diacrylate or propane diol triacrylate.

The matrix-forming composition may further comprise suitable photoinitiators, stabilizers or antiblocking agents.

The swell index of the cured material may be easily determined by measuring the initial volume of the matrix material, immersing the matrix material in a solvent, and measuring the volume of the matrix material after immersion. The swell index is the percent change in volume of the matrix material. Suitable solvents which do not adversely affect the matrix coatings on glass optical

fibers include ethanol and/or isopropanol.

A typical composition for an electron-beam curable inner primary or outer primary (secondary) coating for use according to the invention comprises:

(A) about 0% to about 95% of at least one reactive oligomer;

(B) about 0% to about 95% of at least one reactive diluent;

(C) optionally, about 0 to about 10% of at least one photoinitiator; and

(D) optionally, about 0 to about 10% of at least one additive.

Preferably at least about 10 wt.% of a reactive oligomer, and at least about 10 wt.% of at least one reactive diluent is present.

A typical composition for an electron-beam curable matrix material coating or ink for use according to the invention comprises:

(A) about 10% to about 90% of at least one reactive oligomer;

(B) about 0% to about 80% of at least one reactive diluent;

(C) optionally, about 0 to about 10% of at least one photoinitiator; and

(D) optionally, about 0 to about 10% of at least one additive.

In inks, generally, higher functional diluents and/or

oligomers will be used.

The invention will be further described by the following non-limiting examples.

EXAMPLES

Example I - Ink sample preparation and cure

A white pigmented UV curable ink was prepared by combining 1260 grams clear base resin with 240 grams white pigment mixture followed by filtering with a sintered metal 20 micron mesh filter. The clear base resin was based on a radiation-curable urethane acrylate oligomer prepared from isophorone diisocyanate, 2-hydroxyethyl acrylate, and the polycarbonate polyol (Permanol KM10.1733) with use of phenoxyethyl acrylate (SR 339). The oligomer composition (44.84 wt.%) was mixed with bisphenol-A-ethoxylated diacrylate, SR 349 (48.01 wt.%); ethoxylated nonylphenol acrylate, Aronix M-113 (4.76 wt.%), and Irgacure 184 (2.39 wt.%).

Black pigmented ink was prepared by mixing 1350 grams of the same clear base resin and 150 grams of black pigment mixture.

An electron beam exposure unit was combined with an endless adjustable speed conveyor belt and set for curing of coated films. Samples were 0.5 inches wide and 1 mil (25 microns) thick and were cured on 11 inch long Mylar strips or on glass microscope slides. All of the samples cured after one passage under the electron beam under atmospheric conditions.

Black and white inks were applied to glass microscope slides or Mylar sheets at a thickness of 25 microns. The samples were exposed to 60 kV electron beam radiation (20 Watts, approx. 340 mA) using a EB Raster Scan at 10 feet/min. No discoloration was detected in the underlying substrates. The degree of cure was measured by infrared methods and is provided in Table 1 below. Also, mechanical properties of cured films were measured and are provided in Table 2 below.

Example II - Coating Samples

Two inner primary radiation-curable coatings were prepared, one with photoinitiator and one without (Example II-1-A and Example II-1-B, respectively). Two outer primary radiation-curable coatings were also prepared, one with photoinitiator and one without (Example II-2-A and Example II-2-B, respectively).

The inner primary coating II-1-A was based on urethane acrylate oligomer (about 30 to about 60 wt.%, preferably about 50 wt.%) which can be represented by H-I-PPG-I-PC-I-H, wherein H is 2-hydroxyethyl acrylate, I is isophorone diisocyanate, PC is polyhexylcarbonate (MW 900), and PPG is polypropylene glycol (MW 1,000). Diluent was isodecyl acrylate (14 wt.%) and ethoxylated nonylphenol acrylate (about 15 to about 35 wt.%, preferably about 25 wt.%). A photoinitiator system was used comprising 2-hydroxy-2-methyl-1-phenyl-1-propanone (about 0.2 to about 1.0 wt.%, preferably about 0.75 wt.%)

and bis(2,6-dimethoxybenzoyl)(2,4,4-trimethylpentyl)phosphine oxide (about 0.5 to about 3.5 wt.%, preferably about 2.25 wt.%). Thermal antioxidant (about 0.1 to about 1.5 wt.%, preferably about 0.5 wt.%) and an optional mercaptopropyl trimethoxysilane adhesion promoter (about 0 to about 5 wt.%, preferably about 1 wt.%) were also present. The primary coating II-1-B included the same ingredients as II-1-A but absent the photoinitiator system.

The outer primary coating II-2-A was based on urethane acrylate oligomer (about 30 to about 60 wt.%, preferably about 35 wt.%) which can be represented by H-T-PTGL-T-H, wherein H is 2-hydroxyethyl acrylate, T is toluene diisocyanate, and PTGL is a polytetramethylene glycol (MW 500-4,000, preferably 1,000). Diluent was ethoxylated bisphenol-A-diacrylate (about 30 to about 60 wt.%, preferably about 50 wt.%) and ethoxylated nonylphenol acrylate (about 4 to about 12 wt.%, preferably about 8 wt.%). A photoinitiator system was used comprising optionally 1-hydroxycyclohexylphenol (about 0 to about 4 wt.%, preferably about 2 wt.%) and optionally diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (about 0 to about 6 wt.%, preferably about 1 wt.%). An optional thermal antioxidant (about 0 to about 1 wt.%, preferably about 0.5 wt.%) may also present. The outer primary coating II-2-B included the same ingredients as II-2-A but absent the photoinitiator system.

Example III - Degree of Curing

Eight samples were submitted for ATR-IR infrared analysis of the degree of surface cure including the top surface (exposed to beam) and the bottom surface (resting on substrate). The bottom surface of each sample was examined to determine the through-cure effects. Degree of cure is expressed as percent reacted acrylate unsaturation (% RAU) and is shown in Table 1.

Table 1. Degree of curing.

			% RAU	
Coating ID	Description	Substrate	Top	Bottom
Example II-1-A	inner primary with photo-initiator	Mylar	96	95
Example II-2-A	outer primary with photo-initiator	Mylar	69	67
Example II-1-B	inner primary without photo-initiator	Mylar	97	94
Example II-2-B	outer primary without photo-initiator	Mylar	55	72
Example 1	white ink	Mylar	34	57
Example 1	black ink	Mylar	35	58
Example II-1-B	inner primary without photo-initiator	glass microscope slide	98	68
Example II-2-B	outer primary without photo-initiator	glass microscope slide	68	65

Tensile properties were also determined. The test parameters for determination of tensile properties were: 0.25 inch wide tensile bar specimen using a 2.0 inch gage length with a 1.0 inch/minute strain rate. The modulus of elasticity was calculated using conventional secant determination at 2.5% elongation or least squares determination. The results are presented in Table 2 for each test sample. Example II-1-A was too fragile to test.

Table 2. Tensile Measurement.

Sample	Tensile(MPa)	Elongation	Modulus(MPa)
Example 1	26	4	849
(white)	24	5	766
	26	12	777
	29	5	926
	27	5	871
	29	8	851
	28	5	908
Example 1	23	5	753
(black)	26	4	871
	27	5	893
	27	7	824
	26	8	777
	26	4	818
	24	4	803
Example 2	15	5	462
II-2-A	23	11	622
	22	7	645
	25	13	668
	23	12	622
	19	11	474
	21	6	620

Sample	Tensile(MPa)	Elongation	Modulus(MPa)
Example 2*	0.2	8	1.6
II-1-B	0.8	69	1.6
	0.6	48	1.5
	0.6	48	1.9
Example 2	25	11	726
II-2-B	20	3	769
	21	3	770
	23	13	674
	22	4	701
	23	7	685
	23	6	677
	22	4	716

*Tested coiled up strip

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to those of ordinary skill in the art that various changes and modifications can be made therein without departing from the spirit and scope of thereof.

WHAT WE CLAIM IS:

1. A method of curing at least one radiation-curable layer surrounding an optical fiber substrate comprising the steps of:

   a) applying at least one radiation-curable layer surrounding said optical fiber substrate; and,

   b) substantially curing said at least one layer with about 125 kV or less of electron beam radiation.

2. A method of curing multiple radiation-curable layers surrounding an optical fiber substrate comprising the steps of:

   a) applying one of said multiple radiation-curable layers surrounding said optical fiber substrate; and,

   b) substantially curing said at least one layer with about 125 kV or less of electron beam radiation; and,

   sequentially repeating said step a) said step b) for each of said multiple radiation-curable layers surrounding said optical glass fiber substrate.

3. The method of any one of claims 1-2, wherein said energy is less than about 80 kV.

4. The method of claim 3, wherein said energy is less than or equal to about 60 kV.

5. The method according to any one of claims 1-4, wherein said layer is substantially cured to a

depth of about 25 mm or less.

6. The method according to any one of claims 1-5, wherein the low power electron beam radiation is generated by an apparatus comprising a plurality of electron beam tubes, each tube emitting a strip-like electron through an electron beam permeable, low-Z, gas impermeable window.

7. The method of claim 6, wherein said tubes are arranged in more than one group, each group having different beam energies.

8. The method of claim 6, wherein said tubes are arranged in three groups, each group being arranged at about 120° angles from one another.

9. The method of claim 6, wherein said tubes are arranged in at least two groups, each group being arranged at about 180° angles from another of said groups.

10. The method according to any one of claims 1-9, wherein the apparatus further comprises a means for advancing the optical fiber past said plurality of electron beam tubes.

11. The method according to any one of claims 6-9, wherein the window comprises silicon carbide, silicon nitride, boron nitride or doped silicon.

12. The method according to any one of claims 1-11, wherein said optical fiber substrate is a glass optical fiber.

13. The method according to any one of claims 1-12, wherein at least one layer has been cured by exposing said at least one layer to low power electron beam radiation effective to

substantially cure said at least one layer but substantially avoid degrading said optical fiber substrate.

14. The method according to any one of claims 1-13, wherein said optical fiber substrate comprises a member of the group consisting of glass and thermoplastics.

15. The method according to any one of claims 1-14, wherein said at least one radiation-cured layer comprises a pre-cure composition comprising:
about 0% to about 95% of at least one reactive oligomer;
(C) about 0% to about 95% of at least one reactive monomer;
optionally, about 0 to about 10% of at least one photoinitiator; and
optionally, about 0 to about 10% of at least one additive.

16. The method according to any one of claims 1-15, wherein said at least one layer is an ink layer or a colored outer primary layer.

17. The method according to any one of claims 1-16, wherein said at least one layer comprises an outer primary coating.

18. The method according to any one of claims 1-17, wherein said radiation-cured layer was cured without substantial presence of photoinitiator.

19. The method according to any one of claims 1-14, wherein the at least one radiation-cured layer is a matrix material.

20. The method according to claim 19, wherein said at least one radiation-cured matrix material coating composition comprises:

(A) about 10% to about 90% of at least one reactive oligomer;

(B) about 0% to about 80% of at least one reactive monomer;

(C) optionally, about 0 to about 10% of at least one photoinitiator;

(D) optionally, about 0 to about 10% of at least one additive.

21. The method of any one of claims 19-20, wherein the distance between said electron beam and said at least one matrix material coating composition is about 0.5 cm to about 2 cm, measured from surface of the electron beam window to the surface of said matrix material coating composition.

22. Coated optical fiber or ribbon, obtainable with the method according to any one of claims 1-21.

INTERNATIONAL SEARCH REPORT

Inte ional Application No
PCT/NL 98/00157

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C25/02

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

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	EP 0 145 378 A (SUMITOMO ELECTRIC INDUSTRIES) 19 June 1985 see page 2, line 20 - page 3, line 14 see page 4, line 7 - page 6, line 9 see page 7, line 12 - page 9, line 23	1-5,10, 12-22
Y	---	6-9,11
X	DATABASE WPI Section Ch, Week 8417 Derwent Publications Ltd., London, GB; Class A89, AN 84-103792 XP002068142 & JP 59 045 944 A (KANSAI PAINT CO LTD) see abstract	1-5,10, 12-22
Y	---	6-9,11
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 June 1998	25/06/1998

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INTERNATIONAL SEARCH REPORT

Inte .tional Application No
PCT/NL 98/00157

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 414 267 A (WAKALOPULOS GEORGE) 9 May 1995 cited in the application see column 1, line 1 - column 3, line 29	6-9,11
A	WO 96 18683 A (VETROTEX FRANCE SA ;MOIREAU PATRICK (FR)) 20 June 1996 see claims	1-22

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INTERNATIONAL SEARCH REPORT

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