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(54) OPTICAL TRANSMISSION FIBRES

(71) We, SUMITOMO ELECTRIC INDUSTRIES, LTD., a Japanese company of No. 15, Kitahama 5-chome, Higashi-ku, Osaka-shi, Osaka, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to optical transmission fibres for use in optical communication systems.

Examples of optical communication systems employing coherent light such as a laser are a beam guide system, a space transmission system, and a system using an optical transmission fibre; the optical transmission fibre, the subject of the present invention, is of the type used in the third of these three optical communication systems.

Reference is now made to the accompanying drawings in which:

Figures 1 (a), (b), (c), (d), (e), (f) and (g) are each a cross-section of an optical transmission fibre together with a representation of the distribution of the refractive index thereacross; and

Figure 2 is a cross-section of an optical transmission fibre according to the present invention.

Some of the optical transmission fibres which have so far been proposed are illustrated in Fig. 1:

Fig. 1 (a) shows a clad type multi-mode optical fibre; Fig. 1 (b), a clad type single-mode optical fibre; Fig. 1 (c), an O-guide type optical fibre; Fig. 1 (d), a self-focussing type optical fibre; Fig. 1 (e), a single material type optical fibre; Fig. 1 (f), a clad type having, in part, gradually varying refractive index; and Fig. 1 (g), an O-guide type of similar construction, these last two being combinations of two of the previously men-

tioned types. The term "clad" refers to an outer portion of the fibre, which may be of different refractive index.

From the point of view of minimising optical loss, glass and in particular a glass comprising quartz glass as a basic component are preferred materials for optical transmission fibres.

However, an optical transmission line formed only of a glass cannot be used for practical purposes (an optical transmission fibre formed of glass alone is referred to hereinafter as an optical glass fibre) because of the following four disadvantages:

(A) Firstly, an optical glass fibre has a quite low elongation at break, a quite large bending radius at break and also a quite low impact shock- and twist-resistance. Furthermore, although on average it has a quite high tensile strength these are quite large deviations therein, with the minimum value being quite low. Therefore, such an optical glass fibre has serious limitations in that the fibre is, on the whole, very fragile, has poor flexibility, and will be broken even by slight deformation. Moreover, during manufacture of the optical fibre or in the course of subsequent handling, defects such as fine cracks are easily formed on the surface of the fibre; consequently if an external force is applied to the defective portion or it is deformed, the stress is concentrated upon the defective portion, which results in an increase of the tendency of the fibre to break. Accordingly, such an optical fibre is not resistant to external force applied, or deformation occurring, during the production of an optical transmission line using an individual optical glass fibre or a combination of such fibres, or during the laying of the optical glass fibres into a cable.

(B) Secondly, optical glass fibre used for optical transmission must be very transparent

that is to say, any cause of absorption or scattering of light must be removed from the material as completely as possible. Defects such as fine cracks formed on the surface of the optical glass fibre cause scattering and leaking of light, which has an adverse influence on the efficiency of the optical transmission.

(C) Thirdly, if leaking light is totally reflected at the outermost surface of an optical fibre and returns to the central core or if light enters the central core from the outside, noise occurs in the optical transmission. Consequently it is desirable to minimize the return of leaking light to the inside of the optical fibre by leading the leaking light outside by some means or by preventing the entrance of external light to the inside as much as possible.

(D) Fourthly, in for example a clad type optical fibre as shown in Fig. 1 (a) or (b), it is impossible to focus or concentrate the light energy completely in a core 1 and the remainder of the light energy enters the clad 2. If the core 1 is a body which is ideally transparent to light, no difficulties occur; however, small impurities are usually present in the core 1 or the interface between the core 1 and the clad 2 is slightly uneven, which causes scattering of light: such scattering causes light to leak. When using a single optical glass fibre, such a difficulty can be avoided by allowing the scattered light to be released from the individual fibre, but when using a plurality of optical glass fibres in the form of a cable, the scattered light can enter the adjacent optical glass fibres and consequently the scattered light must be trapped.

Although optical glass fibres have excellent optical transmission properties, it is impossible to put them to practical use because of the foregoing four disadvantages (A), (B), (C) and (D).

An object of this invention is therefore to provide an optical glass fibre in which the above - described disadvantages are reduced or eliminated.

From a study of the results of covering the optical glass fibre with thermoplastic resin composition by means of melt-extrusion we have found that those resins having poor adhesion to glass such as polyethylene, polypropylene, fluorinated ethylene-propylene copolymer and the like have little effect on improving the mechanical strength of the optical glass fibres and, therefore, provide no fundamental solution to the aforesaid problems. Resins such as polyamides, polyesters and the like having polar or functional groups improve its mechanical properties such as tensile strength; tolerance to deformation, for example by bending; flexibility; and elongation: these resins somewhat reduce

the disadvantages of optical glass fibre when coated thereon by melt-extrusion. However, the optical fibres thus coated have very uneven characteristics and the mean values and the minimum values of their mechanical strength are still low although considerably enhanced as compared with those of uncoated optical glass fibre.

When making optical glass fibres into an optical transmission cable, each of the fibres is subjected to repeated operations of twisting, assembling and taking up and is also subjected to great external forces when it is handled, transported and worked during cable laying operations. Resistance to stretching forces is particularly important: the elongation of glass at break is of the order of 0.1%, which is far from enabling it to withstand such external stretching forces. Considering that copper conductors conventionally used for communication lines have an elongation of the order of several tens of a percent, the above value is very low. In addition, it is required that the unit length of an optical transmission cable in an optical transmission system is as much as several hundred to several thousand metres in order to minimize the optical losses at the joints. This necessitates characteristics that are more uniform along its length and that the minimum values in a unit length are required to be as high as possible, rather than the mean values, as in the past. From such point of view, it has been found that a practicable optical transmission cable can hardly be obtained merely by coating the optical glass fibres with the thermoplastic resin by means of melt-extrusion and hence that further improvements in the mean values and the minimum values: flexibility, elongation at break and tensile strength are necessary.

We made a further study of the conditions necessary for coating and baking a solution of a thermoplastic or thermosetting resin composition. It has been found, as a result, that such coating and baking cycles must be repeated several times in order to obtain a film having a thickness of 50 to 200 microns which is considered to be the thickness range necessary to attain the desired properties; this is because the thickness of a film obtained by one coating and baking cycle should usually be restricted to no more than several microns in order to avoid troubles such as blistering. This makes the operation very complicated and requires much equipment. Also, in repeating the cycle for several tens of times, high tensile, torsional, bending and impact stresses are likely to be applied and frequently cause defects such as breaks, cracks and the like in the optical glass fibres. Thus it is necessary for practising this method industrially to reduce the velocity of the line to a much lower extent than that used for coating by melt-extru-

5 sion and to use equipment which has been
made with extremely high accuracy; these
requirements may increase the manufacturing
costs of the equipment significantly and even
make the fabrication of the equipment im-
possible. Further, since the resin composi-
tion must be dissolved or dispersed in
solvent, those resins that can neither be dis-
solved nor dispersed in solvent cannot be
used. From the foregoing it will be appreci-
ated that neither coating by the melt-extru-
sion or by the coating and baking method
has proved to be of much practical value.

10 An optical transmission fibre according to
the invention has a characteristic structure,
namely it comprises an optical glass fibre
having on its surface (a) one or more layers
formed by coating and baking a liquid resin
composition or a solution or a dispersion pre-
pared by dissolving or dispersing in a solvent
a liquid or solid resin composition, and (b)
an outer coating of thermoplastic resin com-
position formed on the or the outermost
layer by melt-extrusion.

15 This transmission fibre can be manufac-
tured by the following method: initially
coating and baking an optical glass fibre with
one or several layers of a liquid resin com-
position, or a solution or dispersion obtained
by dissolving or dispersing a liquid or
solid resin composition in a solvent, and
then melt-extruding one or several layers of
thermoplastic resin composition thereover. By
this method an optical transmission fibre can
be obtained in which the foregoing dis-
advantages (A) and (B) are overcome, which
has much enhanced minimum values with
respect to both its mechanical and optical
properties, which has excellent stability and
which can easily be manufactured. It was
further found that a great advantage is
obtained according to the present invention,
as may be seen in Example 2 to be given
later, in that a tough and flexible optical
transmission fibre can be manufactured using
a resin such as polyethylene or polypropylene
having no polar or functional groups and
therefore poor adhesion to glass.

20 Surprisingly, it was also found that out-
standing improvements in the properties
could be obtained by carrying out the above-
described process for coating and baking the
liquid resin composition immediately after
the melt-drawing of the glass fibre and prior
to contact of the drawn glass fibre with
solid bodies such as guide reels or drums
(that is, in a so-called tandem manner).

25 By means of the present invention, a
coated and baked layer of a resin composi-
tion, preferably of a resin composition having
good adhesion to the glass is formed on
an optical glass fibre and a thermoplastic
resin composition of high elongation and
excellent flexibility is coated thereover by
extrusion, which enables a desired film thick-

ness to be formed in a simple coating and
baking operation and by application of an
outer coating by melt-extrusion and thus pro-
duces an optical transmission fibre having
excellent mechanical strength, flexibility and
high durability when subjected to deforma-
tion.

The reasons for such significant improve-
ment with respect to the above defects and
enhancement in the properties of the fibre
afforded by the present invention are con-
sidered to be as follows:

(1) The viscosity of the resin composi-
tion for coating and baking can be greatly
reduced by the use of a liquid resin com-
position or of a solution or a dispersion
obtained by dissolving or dispersing a liquid
or solid resin composition in a solvent, and
such viscosity can also be lowered signifi-
cantly by increasing the temperature during
baking. This provides much better wetting
of the surface of glass as compared with
the case where the surface is directly covered
with a molten resin composition of extremely
high viscosity, and even when cracks or un-
evennesses are present on the surface of glass
the resin composition can enter to some
extent into them to ensure uniform and
sufficient close contact between the resin
composition and the surface of glass.

(2) The resin composition for coating
and baking preferably contains polar or func-
tional groups which, it is supposed, interact
with the $\equiv\text{S}-\text{OH}$ groups existing on the
surface of glass, for example, by way of
hydrogen bonding to cause strong adhesion,
thereby increasing the adhesive strength due
to a positive composite effect. Also, it may
be that when a thermosetting resin composi-
tion is used as a resin composition for coat-
ing and baking, reactive groups in the mole-
cules of the thermosetting resin may react
with hydroxyl groups existing on the surface
of glass thereby again increasing the adhe-
sion.

(3) When the coating and baking process
for above-mentioned liquid resin composi-
tion is arranged in tandem to the process for
drawing the optical glass fibre, it is considered
that the surface of the glass fibre is kept in a
condition in which it is still clean and
possesses a high surface energy and, there-
fore, is easily wetted with liquid resin com-
position. Accordingly, a coated film very
firmly bonded to the glass surface can be
formed on the said surface by coating and
baking, which protects the surface of the
glass fibre and prevents cracks from grow-
ing on the glass surface thereby enabling
it to maintain the high initial properties
possessed by the glass fibre immediately after
spinning.

(4) As stated above, an optical glass fibre
to which one or more layers of thin coated
film have been applied is still of small dia-

meter, inconvenient to handle and has insufficient strength to withstand being made into a cable; it also has insufficient deformation-resistance and flexibility; however its fragility is much reduced as compared with an uncoated optical glass fibre. In addition, it is conceivable that, as the coated and baked film serves as protection, the adverse effect of atmospheric moisture and dust which is said to decrease the strength of glass fibre can be reduced and also cracks can be kept from forming on the surface during subsequent treatment. Furthermore, it is believed that by first coating and baking a highly adhesive resin and subsequently melt-extruding thereover a highly flexible thermoplastic resin composition, firm bonding can be obtained between the optical glass fibre and the resin composition through the coated and baked layer or layers to impart flexibility to the optical glass fibre: a synergistic effect also results from the combination of the optical glass fibre and the resin composition thereby providing a very tough and flexible optical transmission fibre.

Furthermore, according to the present invention, there can be eliminated the adverse effects of light leaking in between each of the individual optical glass fibres as well as those of reflection at the interface (these disadvantages were previously referred to under (C)) by selecting the refractive index of the resin composition to be coated and baked and of the thermoplastic resin composition to be applied by melt extrusion to be just slightly more than that of the outer portion of the optical glass fibre and that of the thermoplastic resin composition to be applied thereover by melt extrusion.

Referring, for example, to a clad type fibre as shown in Fig. 2, a core 1 is sequentially surrounded on its outer surface with a clad 2, a layer 6 in close contact therewith, formed of a coated and baked resin composition and a layer 7 formed of a thermoplastic resin composition. If the refractive indices of the resin composition layers 6 and 7 are n_6 and n_7 respectively and that of the clad 2 is n_2 , and the resin composition and the glass so selected that the following relationships are satisfied,

$$n_6, n_7 \geq n_2; n_6 \geq n_2;$$

and

$$n_7 \geq n_2$$

then the amount of reflection of light leaking from the clad 2 at the interface between the clad 2 and the resin composition layer 6 is zero or only a little surface reflection. The leaking light is therefore prevented from entering the core 1 thereby eliminating adverse effects such as distortion in pulses.

It can easily be proved by Snell's law that even when n_6 is greater than n_7 the amount of light leaking from the resin composition layer 6 at the interface between the resin composition layer 6 and the resin composition layer 7 is zero or only a little surface reflection only if the relation

$$n_7 \geq n_2$$

is satisfied.

In addition to disadvantages (A) and (B), disadvantage (D), that is, the intrusion of light leaking from one optical glass fibre into others, or the further intrusion of external light to the interior, can be prevented by forming one or more layers of the coating of a material such as carbon black capable of absorbing light of all wavelengths or a material such as a pigment or dye capable of selectively absorbing light of wavelengths to be used for optical transmission.

It is most desirable to overcome both of the related disadvantages (C) and (D) by using such light-absorbing layers and selecting the various components so that the above relationships

$$n_6, n_7 \geq n_2; n_6 \geq n_2;$$

and

$$n_7 \geq n_2$$

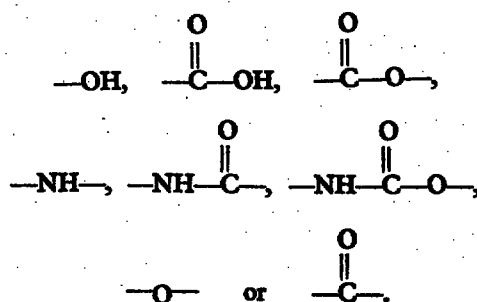
can be satisfied.

The resin compositions for coating and baking used in this invention include one or more of a resin either alone or in admixture with one or more of additive resins, curing agents, curing accelerators, cross-linking agents, reactive diluents, carbon fillers, adhesion improvers, for example, a silane coupling agent and the like. The term "liquid resin composition" used herein includes a resin composition which is liquid at normal temperature, as well as any of the above-described mixtures of one or more of reactive monomers which is a liquid at normal temperature.

In applying and baking these resin compositions, the liquid resin is used as it is or, if the viscosity thereof is high, the resin is dissolved or dispersed in an appropriate solvent: the solid resin is dissolved or dispersed in an appropriate solvent and then used for coating and baking. Among others, those resins compositions having uniform and high adhesion to the glass are preferred for the coating and baking layers and most preferred are those also having uniform and high adhesion to the layer of the thermoplastic resin composition to be provided thereover. The resin used as a main ingredient in the resin composition may be of any type such as thermoplastic or thermo-

(14)

setting types and, from the point of view of adhesion to the glass fibre, may be, for example, a polyester, a polyamide, a polyacetal, a polyvinylacetal, a polysulphone, a polyurethane, a polyether, a polyesterimide, a polyamideimide, a polyimide, a polyacrylate, a polyvinylacetate, an ethylene-vinylacetate copolymer, an ethylene-acrylic acid copolymer, an epoxy resin, an epoxy resin derivative, a phenolic resin, a resorcinol resin, an unsaturated polyester resin, a urea resin, a furan resin, a silicone resin, an alkyd resin, a melamine resin, a diallylphthalate resin or a derivative thereof, those containing polar or functional groups being generally preferred. The term "polar or functional groups" is used to mean



More preferred thermosetting resins among other are epoxy resins, phenolic resins, unsaturated polyester resins, silicone resins, alkyd resins, furan resins, urethane resins and diallylphthalate resins, and more preferred thermoplastic resins are phenoxy resins, polyvinylacetal resins, polyester resins, polyacrylate resins and polyester-imide resins, as well as their derivatives, all of which have excellent adhesion to glass. The excellent adhesion is considered, with respect to the thermosetting resin, attributable to their reactive nature with the —OH groups present on the surface of the glass and it is also supposed that the —OH groups, ester linkages, etc. in the resin act effectively to improve adhesion. Resins of this type have a relatively high elastic modulus of more than 200 kg/mm² and on the other hand a relatively low coefficient of thermal expansion and therefore have properties close to those of glass relative to the effects of external force, heat and the like. It is supposed that they provide a graduation between the glass fibre and the melt extrusion layer of thermoplastic resin, thereby moderating any excess concentration of stress and thermal effect. Particularly, it is found that an epoxy resin, an unsaturated polyester resin which is an oligomer obtained by reacting a glycol with an unsaturated dicarboxylic acid or anhydride thereof, or a phenoxy resin is preferred, from the point of view of the properties of the coated fibre.

Where the coating and baking the liquid

resin composition is carried out in tandem to the drawing of the glass fibre, it is preferred to use an unsaturated polyester resin composition, in particular one containing as a main ingredient an unsaturated polyester resin as just described above. Since the above-described resin compositions have the properties both of high adhesion to the glass (attributable to the epoxy resin) and of fast curing of the unsaturated polyester (due to the reactions of a peroxide and a vinyl monomer), the coating and baking process can be performed rapidly and the properties after said process are similar to those of an epoxy resin. Therefore, in coating and baking such a resin composition immediately after drawing the glass fibre and prior to contact with solid objects such as a guide reel or take up drum, neither significant slowing of the line speed nor the provision of a longer baking furnace is required, thereby enabling the processing to be carried out in compact equipment. These embodiments are illustrated in Examples 7 and 8. In addition to the above-described unsaturated polyester resins, other resin compositions comprising as a main ingredient an epoxy resin, a phenolic resin, a phenoxy resin, a silicone resin, a polyvinylacetal resin or a polyacrylate resin can of course provide similar advantageous effects when used in relation to the tandem system, by employing equipment suited to the baking speed required for the resin and depending upon the baking conditions.

The above-described resins may be blended with each other or with a silane coupling agent such as γ -glycidoxypropyltrimethoxysilane, γ -aminopropyltriethoxysilane, methacrylate chromic chloride, tetraalkyltitanate or a derivative thereof to improve the adhesion between the glass and resin. As may be seen in fact from Example 4, it is found that a resin incorporating a silane coupling agent has better properties than a resin without such a coupling agent.

The thermoplastic resin forming a coated layer 7 shown in Fig. 2 may be constituted by a thermoplastic resin alone or in admixture with one or more of additive resins, inorganic fillers, organic fillers, cross-linking, pigments, agents and dyes, which mixture is capable of being applied as a coating by melt-extrusion (a method comprising melting the resin composition in a screw-type extruder and extruding the molten resin through a wire coating die to apply a coating or a method of melting the resin composition by any method and extruding the same by a gear pump to effect coating).

Almost any thermoplastic resin is suitable for coating by melt-extrusion, the following among others, being preferred: a polyamide, a polyester, a polycarbonate, a polyurethane, a polyurea, a polyhydantoin, a polysulphone, a polyether, a polyesterimide, an ionomer

resin, a polyvinyl resin, a polyethylene, a polypropylene, an ethylene-vinylacetate copolymer, an acrylonitrile - butadiene - styrene terpolymer, a chlorinated polyethylene, an ethylene-acrylic acid copolymer, a urethane rubber, a polychloroprene, an ethylene-propylene rubber and chlorosulphonated polyethylene. All of the above resins have a much greater elongation than a thermosetting resin or glass, and when incorporated in the construction according to the present invention, they are sufficiently secured to the glass fibre through the intermediate layer of resin composition to impart such properties as deformability and flexibility to the glass fibre which itself lacks such properties, resulting in a synergistic composite effect to produce a tough and flexible optical transmission fibre as previously discussed. Furthermore, the refractive index of each of the above-described resin compositions for the coated layers 6 and 7 is higher than the refractive index (about 1.46) of glass comprising quartz as a basic component, and thus the aforesaid disadvantage (C) can be overcome by employing such a resin composition.

An optical transmission cable may be produced by combining a plurality of individual optical glass fibres according to the present invention and each of the constituent fibres in the cable may be distinguished by incorporating pigments, dyes or colouring fillers partially or wholly, in either or both of the resin compositions, or the surface of the optical transmission fibre obtained according to the present invention may be tinted with dye or painted with colouring ink.

In the following Examples of the invention and Comparison Examples, breaking loads and elongation at break were measured using a tensile strength tester (manufactured by Instron Co., U.S.A.). The tensile velocity and the length of the specimens (distance between chucks) were 5 mm/min. and 100 mm respectively, and the number of the specimens used in each Example was twenty-five, the mean values and the minimum values arrived at being shown in Tables 1 and 2. The minimum bending diameter was determined from the average for twenty pieces by measuring the minimum diameter at which the test piece was broken as it was being bent under a no-tension condition. The breaking load, elongation and the minimum bending diameter are shown as values that were indicated when either the optical glass fibre or the coating or both were broken. Usually, optical glass fibres were broken first or both the fibre and the coating were simultaneously broken.

Unless otherwise indicated all parts and percentages are given by weight in the Examples.

EXAMPLE 1

A clad type optical glass fibre of 200 μ diameter containing as a basic ingredient quartz glass was washed with butylcarbitol and then a solution prepared by dissolving phenoxy resin (PKHH, manufactured by Union Carbide Corporation, U.S.A.) in butylcarbitol to a resin content of 20% was coated thereon and baked. The coating was effected in a liquid tank containing the above solution, the fibre being passed through a die of 0.30 mm diameter, and a tubular furnace two metres in length was used for baking at a temperature of 270–330°C. The line velocity was 60 cm/min. and the film thickness formed per coating and baking cycle was 6 μ .

Then to the fibre thus coated and baked was applied a coating of molten Nylon-12 (manufactured by Hüls AG, Germany) by drawing it at a resin temperature of 235°C through a die and then immediately cooling it with water to produce an optical transmission fibre.

The optical transmission fibre thus obtained was very flexible and had such a toughness as not to be broken when bent to a diameter only several times its own diameter; its tensile and bending properties of the optical transmission fibre are shown in Table 1.

EXAMPLE 2

A clad type optical glass fibre of 200 μ diameter containing as a basic ingredient quartz glass was washed with 2-butoxy ethanol, and a solution of epoxy resin (Epikote 828, manufactured by Shell Chemical Co.; "Epikote" is a registered Trade Mark), diaminodiphenylmethane and 2-butoxy ethanol in a weight ratio of 37:11:52 was coated and baked onto said fibre. The coating was effected through a die of 0.30 mm diameter and a tubular furnace two metres in length was used for baking. The coating and baking was effected at a temperature of 220°C–270°C and with a line velocity of 60 cm/min. The film thickness obtained was 10 μ .

Then to the fibre thus coated and baked was applied a coating of low density polyethylene (Sumikathene (registered Trade Mark) E 209, manufactured by Sumitomo Chemical Industries Co.) by extruding it through a tubing type die and point under reduced pressure to produce an optical transmission fibre. The fibre thus obtained was very flexible and was not broken as it was bent to a diameter only several times its own diameter; the tensile and bending properties of the optical transmission fibre are shown in Table 1.

EXAMPLE 3

A clad type optical glass fibre of 200 μ diameter and containing quartz glass as a

basic ingredient was coated with phenolic resin (Sumilit Resin PR-961A, manufactured by Sumitomo Durez Co. Ltd.) and then baked. The coating was effected by directly immersing the fibre in a liquid bath and then taking it up without using a die. The baking was effected in a tubular furnace two metres in length at a temperature of 140—190°C with a line velocity of 20 cm/min. The film thickness produced was 5 μ . To the fibre thus obtained was applied a coating of molten Nylon-12 (Hüls, AG Germany) by drawing it from the nylon at a resin temperature of 235°C and then through a die, and then immediately cooling to produce an optical transmission fibre. The tensile and bending properties of the fibre thus obtained are shown in Table 1.

EXAMPLE 4

A clad type optical glass fibre of about 200 μ diameter and containing quartz glass as a basic ingredient was washed with butylcarbitol. Phenoxy resin (manufactured by Union Carbide Corporation, U.S.A.) was dissolved in butylcarbitol to a resin content of 20% and blended with 3% γ -glycidoxypolytrimethoxysilane, and the blend was coated onto said fibre and baked. The coating and baking were effected by drawing the glass fibre through a die of 0.30 mm diameter in a liquid tank containing the above solution and baked in a tubular furnace two metres in length. One cycle of the coating and baking was effected at a temperature of 270°C—330°C and a line velocity of 60 cm/min. The film thickness obtained was 6 μ .

Then a coating was applied to the fibre by drawing it from molten Nylon-12 (Hüls AG, Germany) through a die and then directly cooling with water to produce an optical transmission fibre.

The optical transmission fibre thus produced was very flexible and tough and it was not broken when bent to a diameter only several times its own diameter; the tensile and bending properties of the optical transmission fibre are shown in Table 1.

EXAMPLE 5

An unsaturated polyester resin composition was coated onto a clad type optical glass fibre of 180 μ diameter and containing quartz glass as a basic ingredient and then baked. The unsaturated polyester resin composition comprised 5 parts of benzoyl peroxide to 100 parts of a mixture of unsaturated polyester resin produced by the reaction of an epoxy resin synthesized from methyl-epichlorohydrin and bisphenol-A with unsaturated carboxylic acid or saturated carboxylic acid, and styrene (Dicklite UE-1150, manufactured by Dainippon Ink & Chemicals Inc.). The resin content of the

above composition was about 70%. Coating was effected by drawing the glass fibre upwardly through a liquid tank containing the above resin composition and subjecting to a felt squeezing. The coated fibre was then passed through a tubular furnace two metres in length and then baked at a temperature of 280—350°C. The line velocity was 12 m/min. The optical glass fibre thus obtained and having a thin coated and baked layer of about 8 μ thickness was coated with Nylon-12 by melt extrusion, using a line velocity of 20 m/min. and a resin temperature of 235°C. The fibre was then passed through a tubing type die and point to shape its outer configuration under a reduced pressure and finally cooled with water.

The tensile and bending properties of the optical transmission fibre thus obtained are shown in Table 1.

EXAMPLE 6

An epoxyacrylate resin composition was coated on a clad type optical glass fibre of about 200 μ diameter and containing quartz glass as a basic ingredient, and then baked. The epoxyacrylate resin composition comprised 5 parts of benzoyl peroxide to 100 parts of a mixture of unsaturated polyester having unsaturated bonds at the ends of the molecules which was produced by the reaction of diglycidylether of bisphenol-A with esters of acrylic acid and methacrylic acid, and styrene (Ripoxy R-840, manufactured by Showa-Highpolymer Co. Ltd.). The coating and making was effected by using same apparatus as in Example 5 at a furnace temperature of 300°C and with a line velocity of 10 m/min. To the optical glass fibre thus obtained having a thin coated and baked layer of about 7 μ in thickness was applied a coating of tetramethyleneterephthalate resin (PBT resin, manufactured by Toray Co.) by melt extrusion, using a line velocity of 30 m/min. and a resin temperature of 245°C. The fibre was then passed through a tubing type die and point to shape its outer configuration under a reduced temperature and then air cooled. The tensile and bending properties of the optical transmission fibre thus obtained are shown in Table 1.

EXAMPLE 7

An unsaturated polyester resin composition (Dicklite UE-1150, manufactured by Dainippon Ink and Chemicals Inc.) as in Example 5 was coated and baked on a clad type optical glass fibre of about 180 μ diameter and containing quartz glass as a basic ingredient, immediately after the drawing of said glass fibre. The material for forming the optical glass fibre was shaped as a rod of 10 mm diameter and it was melted in a high frequency furnace before being drawn to a diameter of 180 μ . When it was vertic-

ally pulled down below said furnace by a distance of about 400 mm, it was passed through a tank containing the above-described liquid resin composition and coated therewith; it was then baked in an electric tubular furnace of about 700 mm in length arranged about 300 mm below the liquid tank. The line velocity was 20 m/min. and the furnace temperature of said baking furnace was 350°C.

The thus-obtained optical glass fibre having a thin coated film of the resin composition (shown as layer 6 in Fig. 2) was not fragile as compared with original glass fibre and was not broken when wound around a rod of 2 mm diameter. Then, the optical glass fibre having the thin coating of the resin composition was coated with a coating of Nylon-12 (Daicel L-1640, manufactured by Daicel Hüls Ltd.) by melt extrusion, using a line velocity of 20 m/min. and a resin temperature of 235°C. The outer configuration of the fibre was then shaped by passing it through a tubing type die and point under a reduced pressure and subsequently water cooled. The tensile and bending properties of the optical glass fibre thus obtained are shown in Table 1: it will be noted that the bending diameter of the fibres was less than 5 mm for all of the tested specimens.

EXAMPLE 8

A composition of epoxyacrylate resin (Ripoxy R-840, manufactured by Showa Highpolymer Co. Ltd.) as in Example 6 was coated and baked on a clad type optical glass fibre of about 200 μ diameter and containing quartz glass as a basic ingredient, immediately after the drawing of said glass fibre. The conditions for the coating and the baking were the same as in Example 7. The thus-obtained optical glass fibre having a thin coated and baked layer (depicted as 6 in Fig. 2) was not at all fragile as compared with the original glass fibre and was not broken when wound around a rod of 3 mm diameter.

Then, the glass fibre having a coated and baked layer thus produced was coated by melt-extrusion with tetramethyleneterephthalate resin (manufactured by Toray Co.) using a line velocity of 30 m/min. and a resin temperature of 245°C and the outer configuration of the fibre was shaped through a tubing type die and point under a reduced pressure and subsequently air cooled. The tensile and bending properties of the optical transmission fibre thus obtained are shown in Table 1: it will be noted that the bending diameter of these fibres was less than 5 mm for all of the tested specimens.

COMPARISON EXAMPLE 1

A clad type optical glass fibre of about 200 μ diameter and containing quartz glass

as a basic ingredient was covered with molten Nylon-12 (manufactured by Hüls AG, Germany) through a die and then immediately cooled with water to produce an optical transmission fibre.

The tensile and bending properties of the resultant transmission fibre are shown in Table 2.

COMPARISON EXAMPLE 2

A clad type optical fibre of about 200 μ diameter and containing quartz glass as a basic ingredient was coated with low density polyethylene (Sumikathene, manufactured by Sumitomo Chemical Industries Co.) by extruding it through a tubing type die and point under reduced pressure to produce an optical transmission fibre.

The tensile and bending properties of the glass fibre thus obtained are shown in Table 2.

COMPARISON EXAMPLE 3

A clad type optical glass fibre of about 200 μ diameter and containing quartz glass as a basic ingredient was coated with tetramethylene terephthalate resin by melt-extrusion, using a line velocity of 30 m/min. and a resin temperature of 245°C. The fibre was then passed through a tubing type die and point to shape its outer configuration under reduced pressure and subsequently air cooled. The tensile and bending properties of the optical transmission fibre thus obtained are shown in Table 2.

COMPARISON EXAMPLE 4

A clad type optical glass fibre of about 200 μ diameter and containing quartz glass as a basic ingredient was coated with phenolic resin (Sumilit Resin PR-961A, manufactured by Sumitomo Durez Co. Ltd.; "Sumilit" is a registered Trade Mark) and then baked. The coating and baking were effected by directly immersing the glass fibre into a tank containing the resin, taking it up without using a die, and then baking in a tubular furnace two meters in length at a furnace temperature of 140–190°C and with a line velocity of 20 cm/min. The coating and baking process was repeated for 10 cycles.

The tensile and bending properties of the optical transmission fibre thus obtained are shown in Table 2.

COMPARISON EXAMPLE 5

The tensile and bending properties of the clad type optical glass fibres containing quartz glass as a basic ingredient and which were subjected to melt drawing under the same conditions as those used for producing the glass fibres used in Examples 1–8 and Comparison Examples 1–4 were measured and the results are shown in Table 2.

TABLE 1

	Outer diam. (μ)	Breaking load* (kg)	Elonga- tion* (%)	Minimum bending diam. (mm)	Coating resins**
Example 1	535	3.34	1.77	5	Nylon-12
		2.05	1.13		phenoxy resin
Example 2	1150	3.35	1.85	5	low density polyethylene
		2.16	1.42		epoxy resin
Example 3	524	3.01	1.57	8	Nylon-12
		2.31	1.25		phenolic resin
Example 4	531	3.83	1.91	4	Nylon-12
		2.36	1.25		phenoxy resin (containing silane) coupling agent
Example 5	556	2.91	1.29	7	Nylon-12
		2.11	0.95		unsaturated epoxy resin
Example 6	565	3.23	1.38	7	tetramethylene-tere- phthalate resin
		2.13	1.00		epoxyacrylate resin
Example 7	469	6.10	2.73	<5	Nylon-12
		2.50	1.22		unsaturated epoxy resin
Example 8	565	4.23	1.80	<5	tetramethylene tere- phthalate resin
		3.02	1.31		epoxyacrylate resin

* Figures in the upper rows represent mean values and in the lower rows represent the minimum values.

** The resins in the upper rows are for the layer 7 and in the lower rows are for the layer 6 in Fig. 2.

TABLE 2

	Outer diam. (μ)	Breaking load* (kg)	Elongation* (%)	Minimum bending diam. (mm)	Coating resin
Comparison Example 1	528	2.54	1.25	10	Nylon-12
		1.34	0.69		
Comparison Example 2	1150	1.68	1.06	17	low density polyethylene
		0.81	0.50		
Comparison Example 3	536	2.73	1.16	10	tetramethylene terephthalate resin
		1.85	0.78		
Comparison Example 4	500	2.54	1.10	11	phenolic resin
		1.86	0.81		
Comparison Example 5	200	1.12	0.53	23	untreated optical glass fibre
		0.72	0.30		

* The figures in the upper rows and the lower rows represent mean values and the minimum values respectively.

Example 1 relates to an optical transmission fibre in which thermoplastic type phenoxy resin is used for the layer 6 and Nylon-12 for the layer 7 and, in this embodiment, both the breaking load and the elongation are improved by 30—40% as compared with the optical transmission fibre of Comparison Example 1 in which Nylon-12 is directly applied by melt-extrusion as a coating onto an optical glass fibre, as well as compared with the optical glass fibre of Comparison Example 5. In particular, the improvement in the minimum values exceeds 50%, showing that the layer 6 significantly contributes to the improvement in stability as well as in the properties of the fibre. In Example 3, thermosetting type phenolic resin is used for the layer 6 and Nylon-12 for the layer 7, and much improvement in the mean and minimum values for both the breaking load and elongation are observable. Each of the fibres can withstand bending up to a diameter several times its own diameter showing that ease of handling is astonishingly improved.

On the contrary, as demonstrated by Comparison Example 4, where the same phenolic resin is coated and baked to form all the layers (refer to Table 2), elongation is as low as 1.10% and flexibility is insufficient, although the breaking load is 2.54 kg which is about the same order as in Comparison

Example 1 in which Nylon-12 is used as a coating; this is considered an insufficient improvement in an optical glass fibre which has the defects of a high modulus and fragility. Surprisingly, it is also demonstrated that while a polyethylene layer having poor adhesion to the glass and which is merely applied as a coating by melt-extrusion onto the glass can neither provide mean values nor minimum values that are acceptable in practice, as shown in Comparison Example 2, the use of a thermosetting type epoxy resin for the layer 6 between the glass and the polyethylene as in Example 2 remarkably improves both the breaking load and the elongation in mean and minimum values, the improvement exceeding 100%.

As stated above, all of the resins used for the layer 6 have —OH groups and have excellent adhesion to the surface of glass and, in addition, they have a high elastic modulus and a low coefficient of thermal expansion, exhibiting characteristics lying between those of the glass and the coating layer 7 which is applied by melt-extrusion. Thus it is apparent that remarkable positive composite effects can be obtained which greatly contributes to the improvements in the properties of the fibre.

Further improvements in the properties are obtained by using the phenoxy resin of Example 1 blended with a silane coupling

agent as shown in Example 4 and it is supposed that presence of the silane coupling agent contributes to the improvement in adhesion.

Examples 5 and 6 illustrate embodiments wherein the resin compositions used for the layer 6 in Fig. 2 comprise epoxy resin modified to introduce unsaturated bonds so that curing can be effected as for unsaturated polyester and, in these embodiments, improvements in all the properties are observable as compared with those in which Nylon-12 or tetramethylene terephthalate resin is applied alone to form the layer 7 in Fig. 2.

It was further surprising that in Examples 7 and 8, wherein the resin compositions are coated and baked in tandem to the drawing of the glass fibre, outstanding improvements in the characteristics are observable and a very excellent fibre can be obtained having both toughness and flexibility. In these embodiments, a high strength is already exhibited after coating and baking the layer and it is considered that the high initial properties of the glass fibre in these respects are preserved by the coating and baking in tandem to the drawing process.

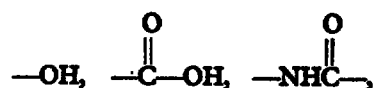
WHAT WE CLAIM IS:—

1. An optical transmission fibre which comprises an optical glass fibre having on its surface (a) one or more layers formed by coating and baking a liquid resin composition, or a solution or a dispersion prepared by dissolving or dispersing in a solvent a liquid or solid resin composition, and (b) an outer coating of a thermoplastic resin composition formed on the or the outermost layer by melt-extrusion.

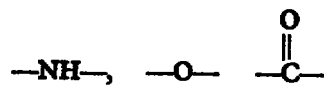
2. A fibre as claimed in Claim 1, wherein the optical glass fibre is coated immediately after the glass fibre has been drawn and before it has come into contact with any other solid object.

3. A fibre as claimed in Claim 1 or 2, wherein the refractive index of the coated and baked resin composition and of the thermoplastic resin composition is equal to or greater than the refractive index of the outer portion of the optical glass fibre.

4. A fibre as claimed in Claim 1, 2 or 3, wherein the resin forming the main ingredient of the resin composition to be coated and baked contains one or more of the following polar or functional groups:



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5. A fibre as claimed in Claim 1, 2, 3 or 4, wherein the resin forming the main ingredient of the resin composition to be coated and baked contains $-\text{OH}$ groups.

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6. A fibre as claimed in any preceding claim, wherein the coated and baked resin composition has an elastic modulus greater than 200 kg/mm^2 .

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7. A fibre as claimed in any preceding claim, wherein the resin forming the main ingredient of the resin composition to be coated and baked is an epoxy resin, an epoxy resin derivative or a phenoxy resin.

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8. A fibre as claimed in any one of Claims 1 to 6, wherein the resin forming the main ingredient of the resin composition to be coated and baked is an unsaturated polyester resin produced by the reaction of a glycol with an unsaturated dicarboxylic acid or unsaturated dicarboxylic acid anhydride.

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9. An optical transmission fibre as claimed in any preceding Claim, wherein the resin composition to be coated and baked contains a silane coupling agent.

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10. An optical transmission fibre as claimed in Claim 1 and substantially as hereinbefore described.

11. An optical transmission fibre substantially as hereinbefore described with reference to any one of Examples 1 to 8 or to Fig. 2 of the accompanying drawings.

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12. An optical transmission cable comprising a plurality of fibres as claimed in any preceding claim.

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agent as shown in Example 4 and it is supposed that presence of the silane coupling agent contributes to the improvement in adhesion.

Examples 5 and 6 illustrate embodiments wherein the resin compositions used for the layer 6 in Fig. 2 comprise epoxy resin modified to introduce unsaturated bonds so that curing can be effected as for unsaturated polyester and, in these embodiments, improvements in all the properties are observable as compared with those in which Nylon-12 or tetramethylene terephthalate resin is applied alone to form the layer 7 in Fig. 2.

It was further surprising that in Examples 7 and 8, wherein the resin compositions are coated and baked in tandem to the drawing of the glass fibre, outstanding improvements in the characteristics are observable and a very excellent fibre can be obtained having both toughness and flexibility. In these embodiments, a high strength is already exhibited after coating and baking the layer and it is considered that the high initial properties of the glass fibre in these respects are preserved by the coating and baking in tandem to the drawing process.

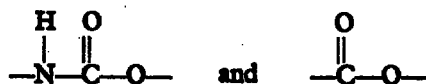
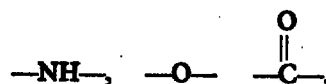
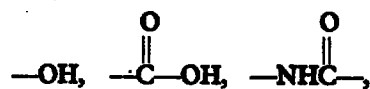
WHAT WE CLAIM IS:—

1. An optical transmission fibre which comprises an optical glass fibre having on its surface (a) one or more layers formed by coating and baking a liquid resin composition, or a solution or a dispersion prepared by dissolving or dispersing in a solvent a liquid or solid resin composition, and (b) an outer coating of a thermoplastic resin composition formed on the or the outermost layer by melt-extrusion.

2. A fibre as claimed in Claim 1, wherein the optical glass fibre is coated immediately after the glass fibre has been drawn and before it has come into contact with any other solid object.

3. A fibre as claimed in Claim 1 or 2, wherein the refractive index of the coated and baked resin composition and of the thermoplastic resin composition is equal to or greater than the refractive index of the outer portion of the optical glass fibre.

4. A fibre as claimed in Claim 1, 2 or 3, wherein the resin forming the main ingredient of the resin composition to be coated and baked contains one or more of the following polar or functional groups:



5. A fibre as claimed in Claim 1, 2, 3 or 4, wherein the resin forming the main ingredient of the resin composition to be coated and baked contains —OH groups.

6. A fibre as claimed in any preceding claim, wherein the coated and baked resin composition has an elastic modulus greater than 200 kg/mm².

7. A fibre as claimed in any preceding claim, wherein the resin forming the main ingredient of the resin composition to be coated and baked is an epoxy resin, an epoxy resin derivative or a phenoxy resin.

8. A fibre as claimed in any one of Claims 1 to 6, wherein the resin forming the main ingredient of the resin composition to be coated and baked is an unsaturated polyester resin produced by the reaction of a glycol with an unsaturated dicarboxylic acid or unsaturated dicarboxylic acid anhydride.

9. An optical transmission fibre as claimed in any preceding Claim, wherein the resin composition to be coated and baked contains a silane coupling agent.

10. An optical transmission fibre as claimed in Claim 1 and substantially as hereinbefore described.

11. An optical transmission fibre substantially as hereinbefore described with reference to any one of Examples 1 to 8 or to Fig. 2 of the accompanying drawings.

12. An optical transmission cable comprising a plurality of fibres as claimed in any preceding claim.

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