

PATENT SPECIFICATION

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(54) OPTICAL FIBRES

(71) We, CORNING GLASS WORKS, a corporation organised and existing under the laws of the State of New York, United States of America, of Corning, New York, United States of America, 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 fibres.

High capacity communication systems operating around 10^{15} Hz are needed to accommodate future increases in communication traffic. These systems are referred to as optical communication systems since 10^{15} Hz is within the frequency spectrum of light. Optical waveguides, which are the most promising medium for transmission as such frequencies, normally consist of an optical fibre having a transparent core having a refractive index n_1 surrounded by transparent cladding material having a refractive index n_2 which is less than n_1 .

It has been known for some time that light can be propagated along a transparent fibre structure having a refractive index that is greater than that of its surroundings, and clad fibres have been employed to transmit light over relatively short distances. The numerical aperture (NA) of such a fibre, which is a measure of the light gathering ability thereof, can be approximated by:

$$NA = \sqrt{2n\Delta} \quad (1)$$

where n is the average refractive index of the core and cladding and Δ is the refractive index difference between the core and cladding. In conventional optical fibres Δ is made quite large so that the NA is large, and therefore the fibre is capable of gathering a relatively large amount of light emitted by a source.

The stringent optical requirements placed on the transmission medium to be employed in optical communication systems has negated the use of conventional glass fibre optics, since attenuation therein due to both scattering and

impurity absorption is much too high. Thus, unique methods had to be developed for preparing very high purity glasses in fibre optic form. Various methods employing the flame hydrolysis technique for forming glass optical waveguide fibres are taught in U.S.A. Patents Nos. 3,711,262; 3,737,292; 3,737,293 and 3,826,560, the latter patent being directed to the formation of gradient index fibres. In accordance with one embodiment of the flame hydrolysis process a plurality of constituents in vapour form are entrained in a gaseous medium in predetermined amounts and thereafter are hydrolyzed in a flame to form a soot having a predetermined composition. The soot is applied to the surface of a rotating cylindrical starting member. After a first layer of soot is deposited to form the core glass, the composition of the soot is changed to form the cladding glass. Heretofore, the soot was either sintered as deposited, or it was sintered in a subsequent operation. After the starting member is removed, the resulting cylindrical hollow redraw blank is heated to a temperature at which the material has a low enough viscosity for drawing and is drawn to reduce the diameter thereof until the inner walls of the hollow member collapse. Continued drawing further reduces the fibre diameter until an optical waveguide fibre having the desired dimensions is formed. In accordance with another embodiment of the flame hydrolysis process the soot is deposited on the inner surface of a glass tube, and the resultant structure is drawn into a fibre.

The value of Δ has been maintained relatively small in optical waveguides for a number of reasons. The cladding of low loss optical waveguides has usually been formed of a high purity glass such as silica, whereas the core has been formed of the same purity glass to which a sufficient amount of dopant material has been added to increase the refractive index of the core to a value greater than that of the cladding. Optical waveguides initially formed by the flame hydrolysis process employed multivalent metal oxides such as titanium

oxide, tantalum oxide and the like as the dopant material. An inherent problem of such waveguides was the limitation of dopant material to no more than about 15 wt.%. Although fused silica has excellent light transmission qualities in that absorption and intrinsic scattering of light thereby is exceptionally low, the addition of an excessive amount of the aforementioned multivalent metal oxide dopant material to increase the refractive index would cause absorption of light energy and intrinsic scattering of light to increase to undesirable levels.

Pure germania also has excellent light transmission qualities in that its absorption and intrinsic scattering of light is exceptionally low. Moreover, the refractive index of germania is sufficiently greater than that of silica so that germania can be employed as a dopant to increase the refractive index of silica. Initial attempts to utilize the flame hydrolysis process to form germania-doped silica fibres were unsuccessful since less than 1 wt.% of germania appeared in the fibre regardless of the amount of germanium tetrachloride supplied to the hydrolyzable mixture. It is theorized that the combustion flame temperature, combined with the overall furnace temperature of 1750—1850°C. employed in those methods, is sufficiently high so that germania tends to volatilize rather than vitrify. Available vapour pressure data tends to support such a theory. However, glasses containing up to 100 wt.% high purity germania can be produced by the method disclosed in our Patent Specification No. 1,415,141 which claims a fused oxide glass, being either a tellurate glass or a glass comprising at least one oxide selected from GeO_2 , P_2O_5 and Sb_2O_3 , comprising GeO_2 , P_2O_5 , Sb_2O_3 or TeO_2 in an amount in excess of 1.0% by weight, and having a cation impurity level, as hereinbefore defined, not exceeding 10 ppm, by weight. That patent specification discloses glasses having a high germania content which can be produced by the flame hydrolysis process by depositing the oxide particles as a porous vitreous preform and then consolidating this porous preform to a solid nonporous body. The temperature must not exceed about 1600°C. in any case and should be maintained, during consolidation, within a range varying between the minimum consolidation temperature of the glass being produced and about 200°C. thereabove.

It was found that by maintaining process temperature below those that would cause volatilization of GeO_2 , step type optical waveguide fibres comprising germania doped cores could be formed. However, the numerical apertures of such fibres could not exceed about 0.2 since only a limited amount of GeO_2 could be incorporated into the fibre core due to a mismatch of core-cladding characteristics such as thermal coefficient of expansion and softening point temperature. Consider, for

example, an attempt to fabricate by the flame hydrolysis process an optical waveguide fibre having a core comprising 20 wt.% GeO_2 and 80 wt.% SiO_2 . The coefficient of expansion of such a core glass is about 19×10^{-7} per degree C, while the coefficient of thermal expansion of a pure fused silica cladding is about 6×10^{-7} per degree C, and the core-cladding expansion mismatch of about 13 points would probably cause the soot preform to crack during the soot consolidation process. The addition of about 13—18 wt.% B_2O_3 to the SiO_2 cladding glass will increase the expansion coefficient thereof to a value within acceptable limits so that preform breakage can be avoided. However, as a consequence of the addition of B_2O_3 to the cladding glass, the draw temperature of the cladding glass will be between 50°C. and 210°C. below that of the core glass, which is about 1800°C. With this kind of viscosity difference, fibre diameter control becomes a severe problem. Thus, optical waveguide fibres, wherein germania is employed as the refractive index increasing dopant material in the core, have had relatively limited Δ values.

The small Δ values of optical waveguides has resulted in numerical apertures that are much smaller than those of conventional optical fibres. Whereas the numerical apertures of commercial optical fibres or light pipes of the conventional type may be as high as about 0.6, the numerical apertures of optical waveguides have usually been between about 0.15 and 0.2.

Optical waveguides are often grouped into cables or bundles to provide redundancy in case of fibre breakage and to transmit a greater amount of the light generated by a source. Attenuation γ due to random fibre bends, which can be caused by the cabling process, is given by the equation:

$$\gamma = \frac{c}{\Delta} \frac{a^{2p}}{\Delta} \quad (2)$$

where c and p are parameters related to the geometry of the random bends and fibre index gradient and a is the fibre core radius. Examination of equation 2 shows that the distortion loss γ can be reduced by decreasing the core radius, increasing Δ , or decreasing p and c by appropriate fibre packaging. The present invention has resulted from an attempt to decrease fibre loss due to random bends by increasing Δ . Because of the relationship set forth in equation 1 such fibres will also exhibit an increased NA.

It is an object of this invention to provide an economical and more easily formed optical waveguide fibre that overcomes the heretofore noted disadvantages.

Another object of this invention is to provide an optical waveguide fibre having a high numerical aperture.

A further object of this invention is to provide an optical waveguide in which both the thermal coefficient of expansion and the softening temperature of the core are compatible with those of the cladding regardless of the difference between the refractive indices of the core and cladding.

According to this invention, there is provided an optical fibre comprising a cladding layer formed of high purity glass, and a core of high purity glass containing an amount of P_2O_5 and GeO_2 to provide a refractive index greater than that of said cladding layer, said core glass having a cation impurity level not exceeding 10 parts per million of transition elements.

The waveguide of this invention is an improvement over germania doped waveguides which have recently been employed in an attempt to provide waveguides of increased numerical aperture. The partial substitution of P_2O_5 for GeO_2 in the GeO_2 - SiO_2 glass system results in a decrease in the softening point temperature with substantially no change in expansion coefficient. Depending upon the amount of P_2O_5 and GeO_2 in the resultant glass, there is often an increase in refractive index as compared with the corresponding GeO_2 - SiO_2 glass which contains the same amount of SiO_2 . These features are advantageous in that they permit high NA optical waveguide fibres to be fabricated with less difficulty than was heretofore encountered. By adjusting the ratio of GeO_2 to P_2O_5 in the core glass of an optical waveguide fibre the softening point temperature of the core glass can be made compatible with that of the cladding glass. Moreover, the waveguides of the present invention possess the advantages of germania doped fibres, viz., they are strong; they do not absorb an excessive amount of transmitted light; and they do not require a post-drawing heat treatment as in the case of titania containing fibres.

Some preferred embodiments of this invention are illustrated in the accompanying drawings in which:

Figure 1 is an oblique view of an optical waveguide in accordance with this invention.

Figure 2 is a sectional view taken at lines 2-2 of Figure 1.

Figure 3 is a ternary diagram in which refractive index is plotted as a function of wt.% composition in the P_2O_5 - GeO_2 - SiO_2 system.

Figure 4 is a graph wherein linear expansion coefficient (25-200°C) is plotted as a function of weight percent oxide in silica for both the B_2O_3 - SiO_2 and GeO_2 - SiO_2 systems.

Figure 5 is a graph wherein softening point temperature at η equals $10^{7.6}$ is plotted as a function of weight percent GeO_2 , P_2O_5 , or B_2O_3 for glasses in the GeO_2 - SiO_2 , P_2O_5 - SiO_2 and B_2O_3 - SiO_2 systems.

Figure 6 is a graph wherein refractive index is plotted as a function of weight percent GeO_2 for glasses in the GeO_2 - SiO_2 system.

It is to be noted that Figures 1 and 2 of the drawings are illustrative and symbolic of the invention, and there is no intention to indicate scale or relative proportions of the elements shown therein. Further, it is to be noted that the present invention expressly contemplates both single mode and multimode optical waveguides regardless of any specific description, drawing, or example set out herein. The present invention also contemplates optical waveguides having cores with either a constant or gradient index of refraction.

Referring to Figures 1 and 2, there is shown an optical waveguide 10 having a cladding layer 12 and a core 14. According to this invention the material of cladding layer 12 is relatively high purity glass and the material of core 14 is high purity glass containing an amount of GeO_2 and P_2O_5 sufficient to increase the refractive index of the core glass to a value higher than that of the cladding glass. In some optical waveguides the cladding does not exist as a distinct layer, the optical characteristics of which differ markedly from those of the core or adjacent layer. U.S.A. Patents Nos. 3,647,406 and 3,785,718, disclose optical waveguides wherein the refractive index gradually decreases from a relatively high value at the core to a lower value at the fibre surface. Whereas the cladding of an optical fibre conventionally comprises a layer of constant refractive index, it may be a layer in which the refractive index continuously changes in a decreasing manner, and indeed, the cladding may contain a region having a refractive index that is higher than the next adjacent layer of smaller radius but having a lower refractive index than the core. A few embodiments of this latter mentioned type of fibre are disclosed in said patent No. 3,785,718. Therefore, as used herein, the term cladding means that outer region of a fibre wherein an insignificant amount of power is propagated.

As will be hereinafter described in greater detail, the ratio of P_2O_5 to GeO_2 is selected to provide a core glass having a softening point temperature that is compatible with that of the cladding glass. Since the core glass portion of a redraw blank produced by the flame hydrolysis process contains a hole that must be closed, the core glass softening point temperature is preferably up to about 50°C. lower than that of the cladding glass so that the core glass will more readily flow and close the hole during the fibre forming process.

A further advantage resulting from the substitution of P_2O_5 for a portion of the GeO_2 in binary GeO_2 - SiO_2 glasses is evident from Figure 3 wherein refractive index is plotted as a function of wt.% composition in the P_2O_5 - GeO_2 - SiO_2 system. It was unexpectedly found that the substitution of P_2O_5

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5 for some of the GeO_2 in a germania silicate glass can result in a ternary glass having an increased refractive index even though the refractive index of P_2O_5 is lower than that of GeO_2 . Moreover, such substitution results in very little change in expansion coefficient. From Figure 3 it can be seen that those glasses comprising less than 70 wt.% SiO_2 exhibit a discernible change in refractive index when P_2O_5 is substituted for some of the GeO_2 . It is further noted that for any given SiO_2 level in the range between 0 and 70 wt.% SiO_2 the refractive index is highest when the amount of P_2O_5 present is 40—60 wt.% of the total amount of dopant ($\text{P}_2\text{O}_5 + \text{GeO}_2$).

15 It may be desirable to substitute P_2O_5 for some of the GeO_2 in a germania silicate core glass even if the refractive index of the

resultant glass is the same as that of the germania silicate glass since P_2O_5 is less expensive than GeO_2 . For example, the refractive index of a glass comprising 56.4 wt.% SiO_2 and 43.6 wt.% GeO_2 is about 1.5. Even though the refractive index of a glass comprising 56.4 wt.% SiO_2 , 7.4 wt.% GeO_2 and 36.2 wt.% P_2O_5 is also about 1.5, this latter mentioned glass would be much less expensive than the former due to the substitution of P_2O_5 for most of the GeO_2 .

Table I compares various properties of glasses in the GeO_2 — SiO_2 — P_2O_5 system with those of the GeO_2 — SiO_2 system, the wt.% SiO_2 being the same in both systems, and thus reveals some of the effects resulting from a partial substitution of P_2O_5 for GeO_2 in germania silicate glasses.

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TABLE I
Properties of P_2O_5 - GeO_2 - SiO_2 Glasses

Glass	Composition (wt. %)		P_2O_5	Refractive Index n	Refractive Index n'	Δn	Softening Temperature ($^{\circ}C$)	Annealing Temperature ($^{\circ}C$)
AA	89.2	0	10.8	1.620	1.608	0.012	660	—
AB	82.7	0	17.3	1.628	1.608	0.020	690	—
AC	78.6	0	21.4	1.632	1.608	0.024	715	—
AD	93.2	6.8	0	1.594	—	—	925	556
AE	82.3	17.7	0	1.563	—	—	930	571
AF	79.4	20.6	0	1.558	—	—	1040	632
AG	58.7	25.7	15.6	1.554	1.546	0.008	817	618
AH	60.1	26.8	13.1	1.552	1.544	0.008	822	613
AI	61.8	29.6	8.6	1.546	1.537	0.009	875	603
AJ	29.4	33.7	36.9	1.546	1.531	0.015	890	759
AK	35.9	34.1	30.4	1.542	1.531	0.011	863	721
AL	48.0	34.6	17.4	1.538	1.530	0.008	830	652
AM	41.0	36.0	23.0	1.541	1.529	0.012	843	678
AN	17.3	40.7	42.0	1.533	1.521	0.012	900	776
AO	23.6	43.2	33.2	1.533	1.518	0.015	—	762
AP	30.4	45.4	24.2	1.528	1.515	0.013	878	725
AQ	36.6	45.5	17.9	1.524	1.515	0.009	895	685

TABLE I (Continued)

Properties of P_2O_5 - GeO_2 - SiO_2 Glasses:

Glass	Composition (wt. %)		P_2O_5	Refractive Index n	Refractive Index n'	Δn	Softening Temperature ($^{\circ}C$)	Annealing Temperature ($^{\circ}C$)
AR	43.1	46.3	10.5	1.520	1.513	0.007	996	639
AS	13.7	46.6	39.7	1.520	1.513	0.007	900	709
AT	12.6	51.7	35.7	1.510	1.505	0.005	897	704
AU	7.6	52.8	39.6	1.506	1.505	0.001	890	649
AV	18.6	53.2	28.2	1.508	1.504	0.004	914	731
AW	25.9	54.6	19.5	1.508	1.502	0.006	951	704
AX	7.4	56.4	36.2	1.500	1.500	0.000	897	—
AY	0	62.9	37.1	1.488	1.491	-0.003	932	691
AZ	0	64.0	36.0	1.488	1.490	-0.002	932	—
BA	23.0	65.4	11.6	1.490	1.489	0.001	1131	710
BB	0	66.4	33.6	1.484	1.487	-0.003	968	611
BC	22.9	66.7	9.4	1.488	1.485	0.005	1158	731
BD	15.0	66.7	18.3	1.490	1.487	0.003	1055	708
BE	7.7	67.7	24.6	1.490	1.485	0.005	996	690
BF	13.2	81.6	5.2	1.471	1.471	0.000	—	—
BG	7.2	82.9	9.9	1.470	1.470	0.000	1270	853
BH	11.3	84.8	3.9	1.475	1.470	0.005	1402	—

TABLE I (Concluded)

Properties of P_2O_5 - GeO_2 - SiO_2 Glasses

Glass	Composition (wt. %)	P_2O_5	Refractive Index n	Refractive Index n'	Δn	Softening Temperature ($^{\circ}C$)	Annealing Temperature ($^{\circ}C$)
BI	5.1	91.4	1.464	1.464	0.000	1268	937
BJ	0	90.6	1.464	—	—	1330	888
BK	0	94.0	1.460	—	—	1403	938
BL	0	100.0	1.458	—	—	1585	1050
BM	0	0	1.507	—	—	—	—
BN	100.0	0	1.608	—	—	867	526

The compositions set forth in Table I were made by the following processes. Glasses AA to BE, BM and BN were made using conventional melting techniques. Weighed amounts of the batch were mixed and melted in 500 cc platinum crucibles for 6—10 hours in an electric furnace at $1650^{\circ}C$. After melting, the glasses were annealed at the annealing temperature for 3 to 4 hours in the crucible and cooled at furnace rate to room temperature. Glass samples were then core drilled from the crucible, and specimens for viscosity and expansion measurements were prepared therefrom.

Glasses BF to BL, which contain over 80 wt. percent SiO_2 , were prepared by the flame hydrolysis technique, phosphorus trichloride, germanium tetrachloride and silicon tetra-

chloride being employed as sources for P_2O_5 , GeO_2 , and SiO_2 , respectively. After the soot blanks were consolidated, specimens for various property studies were cut, ground and polished.

In order to evaluate the effect on refractive index due to the substitution of P_2O_5 for GeO_2 in GeO_2 - SiO_2 glasses, the refractive indices n' of the corresponding glasses of the GeO_2 - SiO_2 system containing the same amount of SiO_2 are also listed in Table I. The change in refractive index due to substitution of P_2O_5 is tabulated as Δn . Refractive index measurements were obtained at the sodium D-

line.

It can be seen that Δn is positive for all germania-containing glasses. The refractive index of P_2O_5 glass being lower than that of

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GeO₂ glass, a positive value of Δn suggests that the increase is not due simply to ideal mixing of the two substances. It is believed that this increase in index arises because of a change in coordination number of some of the Ge atoms from 4 to 6. Phosphorus pentoxide exists in the form of P₂O₅ molecules which are linked together by weak van der Waals forces. The P₂O₅ molecule is made up of four identical tetrahedra with the phosphorus atoms at the center. These tetrahedra are interconnected such that there is one non-bridging oxygen in each tetrahedra. It is hypothesized that these non-bridging oxygen atoms produce the change in coordination number of germanium atoms and hence increase the refractive index of the glass.

The refractive indices of pure SiO₂ glass, GeO₂ glass and P₂O₅ glass are 1.458; 1.608 and 1.507, respectively, as given in Table I. The refractive indices of those binary glasses of Table I which do not contain SiO₂, such as glasses AA through AC, are significantly higher than either a P₂O₅ glass or a GeO₂ glass, a fact in support of the above-mentioned theory. It is noted that the value of Δn in these glasses increases with an increase in P₂O₅ content.

In general, Δn decreases with increasing SiO₂ content as evidenced by glasses BE through BI. This may be due to the smaller number of germanium atoms available for a change in coordination number. However, although the change in Δn is less for these high SiO₂ content glasses, it is not negative in GeO₂ containing glasses. Since the refractive indices of P₂O₅—SiO₂ glasses, viz. glasses AY, AZ and BB, are lower than corresponding GeO₂—SiO₂ glasses it is evident that the addition of P₂O₅ to GeO₂—SiO₂ glasses increases the refractive indices thereof even at low GeO₂ concentrations.

Thermal expansion measurements which were made on a differential dilatometer, were generally made at a heating rate of 600°C/hour. The linear expansion coefficient was calculated for the 25—300°C. range. The expansion coefficient of each ternary glass listed in Table I was measured and compared with the corresponding glass of the GeO₂—SiO₂ system containing the same amount of SiO₂. The change in expansion coefficient for each comparison was found to be less than $\pm 5 \times 10^{-7}$ which was smaller than the experimental error in these measurements. Thus, the substitution of P₂O₅ for GeO₂ in the GeO₂—SiO₂ glass system does not result in any appreciable change in expansion coefficient.

The softening point temperature, that temperature at which the viscosity of a glass is 10¹³ poise, is also listed in Table I. It is seen that the partial substitution of P₂O₅ for GeO₂ results in a softening point temperature that is lower than that of the corresponding GeO₂—SiO₂ glass. Also listed in Table I is the

annealing temperature, that temperature at which the viscosity of the glass is 10¹³ poise. The annealing temperature increases with increasing P₂O₅ content in the glass, an effect contrary to that caused by the addition of P₂O₅ on softening temperature. It is possible that due to a change in coordination number of some of the Ge atoms from 4 to 6, the glass has a rigid structure at the lower temperatures in the annealing range. At the higher temperatures in the softening temperature range, these bonds are broken, thereby resulting in a lower viscosity. The softening point temperature is of interest since fibres are drawn at a viscosity near the softening point temperature viscosity. A fibre is more easily drawn if the softening point temperatures of the core and cladding glasses are closely matched, the core glass preferably having a viscosity that is about 1—4 times lower than the cladding glass at the drawing temperature.

Because of the heretofore noted properties of glasses in the GeO₂—SiO₂—P₂O₅ system, optical waveguides embodying such glasses are more easily formed and have higher numerical apertures than prior art waveguides. In general, the cladding may consist of a high purity optical glass such as silica or a silica containing glass. The core glass comprises a high purity optical glass containing an amount of GeO₂ and P₂O₅ that is sufficient to provide a refractive index necessary to obtain the desired NA. The relative amounts of GeO₂ and P₂O₅ are selected to render the softening temperature of the core compatible with that of the cladding. It has been found that in order to avoid excessive light attenuation, the core glass of the waveguide of the present invention must have a cation impurity level not exceeding ten parts per million of transition elements. The preferred cladding material is a silicate glass containing an amount of B₂O₃ that is sufficient to render the expansion coefficient of the cladding compatible with that of the core. The expansion coefficient of the core may equal that of the cladding, but it preferably exceeds that of the cladding by up to about 5×10^{-7} per degree C. to provide a compressive force in the cladding which strengthens the resultant waveguide fibre; however it may tolerably exceed that of the cladding by about 15×10^{-7} per degree C.

To design an optical waveguide fibre in accordance with the present invention the required fibre NA is first determined. Knowing the type of cladding material to be employed, the cladding refractive index n_2 is known. For example, if the cladding material is SiO₂ doped with B₂O₃, n_2 is taken to be 1.458, the refractive index of silica. Using the well known relationship

$$N = \sqrt{n_1^2 - n_2^2} \quad (3)$$

the core refractive index n_1 is determined.

The total dopant level of GeO_2 and P_2O_5 can be determined from Figure 3. If, for example, n_1 is determined to be 1.48, the core glass will contain about 74 wt.% SiO_2 and 26 wt.% (GeO_2 and P_2O_5).

Since the expansion of a GeO_2 - SiO_2 glass is substantially the same as GeO_2 - SiO_2 - P_2O_5 glass having the same silica content, Figure 4 can be used to determine the amount of B_2O_3 that must be present in the cladding glass to match the expansion coefficient of the cladding to that of the core. For example, a core glass containing about 30 wt.% dopant material (GeO_2 plus P_2O_5) has an expansion coefficient of about 25×10^{-7} per degree C., which corresponds to a cladding glass of 21 wt.% B_2O_3 and 79 wt.% SiO_2 . Since the expansion coefficient of the core may be up to 5 points higher than that of the cladding, the cladding glass may contain between about 16-21 wt.% B_2O_3 , thereby providing an expansion coefficient between 20 and 25×10^{-7} per degree C.

The softening point temperature of the cladding glass is determined from curve 60 of Figure 5. Due to the high softening point temperatures of germania silicate glasses, as illustrated by curve 62, a germania silicate core glass will be harder than the cladding glass at fibre drawing temperatures. However, curve 64 illustrates the fact that the softening point temperatures of P_2O_5 - SiO_2 glasses are much lower than those of the germania silicate system. It has been found that there is no interaction between P_2O_5 and GeO_2 when these two oxides are present together, insofar as softening point temperature is concerned. Moreover, since curve 62 is linear, the following relationship can be used for calculating the softening temperature T_{12} of the ternary glass $x\text{P}_2\text{O}_5$ - $y\text{GeO}_2$ - $z\text{SiO}_2$:

$$T_{12} = T_1 - yS \quad (4)$$

where T_1 is the softening point temperature of the binary glass $x\text{P}_2\text{O}_5$ -($y+z$) SiO_2 as determined from curve 64 of Figure 6, and S is the decrease in softening temperature of the binary GeO_2 - SiO_2 glass per percent addition of GeO_2 , which has been determined from curve 62 to be 4.52. The total amount of dopant ($x+y$), as mentioned hereinabove, is that amount necessary to provide a refractive index n_1 . By a trial and error procedure different values of x can be assumed until the desired softening temperature is obtained. It is noted that a ternary graph of softening point temperature would provide a direct reading of temperature T_{12} , thereby eliminating this trial and error process.

Referring to Figure 3, refractive index is relatively constant with respect to SiO_2 content for concentrations of SiO_2 over 70 wt.%. However, refractive index is nonlinear with P_2O_5 or GeO_2 concentrations in that

region of Figure 3 wherein SiO_2 content is less than 70 wt.%. To select a core composition in this latter mentioned region a trial and error method may have to be employed in order to optimize refractive index, expansion and softening point temperature of the core and cladding glasses.

Due to the high purity glass which must be employed for the core, the redraw blank is prepared by a flame hydrolysis process similar to that disclosed in the aforementioned U.S.A. patents Nos. 3,711,262; 3,737,292; 3,737,293 and 3,826,560. In a manner which is now conventional for making low loss glass optical waveguide fibres, a layer of glass soot is deposited on a cylindrical glass starting member by means of a flame hydrolysis burner to which fuel gas and oxygen or air are supplied to produce the flame. Liquid constituents required to form the glass soot are stored in containers having controlled temperatures. A suitable gaseous medium such as oxygen, nitrogen or the like is bubbled through the liquids where predetermined amounts of vapour from the liquids are entrained therewith and carried to the flame. The amount of each constituent supplied to the flame is determined by the temperature of liquid and the rate of flow of the carrier gas through the liquid. Some constituents, which are in gaseous form, are supplied directly to the flame. In the flame the constituents are oxidized to form glass soot that is directed toward the starting member. For a step-index waveguide the first applied soot layer, which is to form the core, has a homogeneous composition. To form a gradient index waveguide the flow rate of at least one of the constituents is varied as taught in U.S. Patent No. 3,826,560. After the first soot layer reaches a predetermined thickness the composition is changed, and a second soot layer, which will form the waveguide cladding material, is deposited. The first soot layer can be consolidated prior to depositing the second soot layer, or both soot layers can be simultaneously consolidated. In view of the volatility of GeO_2 and P_2O_5 , the precautions set forth in our aforementioned Patent No. 1,415,141 pertaining to soot deposition and consolidation should be taken. Any glass layer containing GeO_2 and P_2O_5 should be produced by depositing the oxide particles as a porous vitreous body and then consolidating this porous soot preform to a solid nonporous body. The temperature of both the flame and the atmosphere surrounding the preform should be low enough that the glass remains in soot form rather than consolidating during deposition from the flame. Moreover, the consolidation temperature must not exceed about 1600°C and should be maintained within a range varying between the minimum consolidation temperature of a particular glass and about 200°C thereabove. The starting member is removed, and the

resultant hollow redraw blank is heated to a temperature near the softening point temperature of the material thereof whereby the viscosity of the material is low enough for drawing. The redraw blank is then drawn to reduce the cross-sectional size thereof and to close the hole in the centre thereof. The drawing process is continued until the desired cross-sectional dimensions are achieved. Optical fibres of the type to which the present invention pertains are generally useful at wavelengths between about 450 and 1350 nm. To be commercially acceptable, such fibres must exhibit an attenuation less than 100 dB/km between 800 and 900 nm. Since fibres having an attenuation less than 10 dB/km between 800 and 900 nm have been produced in accordance with the present invention, they are useful as the light propagating medium in optical communication systems.

A specific example of designing an optical waveguide of the present invention is as follows. Based upon such considerations as the type of light source to be employed and the types of bends to which a fibre will be subjected, a specific numerical aperture is selected. This example will assume that the fibre must have a numerical aperture of 0.24. It will also be assumed that the cladding material is a boro-silicate glass which has a refractive index of about 1.458. From equation 3, the refractive index n_1 of the core is determined to be 1.477.

To illustrate the primary advantage of the waveguide of the present invention, the difficulties encountered in forming a prior art waveguide having a germania silicate core will initially be considered. From Figure 6 it is determined that the core glass should consist of 23 wt.% GeO_2 to provide a binary GeO_2 - SiO_2 glass having a refractive index of 1.477. Referring to Figure 4, the expansion coefficient of such a glass is about 20×10^{-7} per degree C. A pure SiO_2 cladding should not be employed with a core containing 23 wt.% GeO_2 since the expansion mismatch between the core and cladding would render it difficult to consolidate the soot preform without it breaking. Thus, a borosilicate cladding having a roughly matching thermal expansion coefficient is selected. From Figure 4 it is determined that a cladding glass of 12 wt.% B_2O_3 , 88 wt.% SiO_2 has an expansion coefficient of about 17×10^{-7} per degree C. The core having an expansion coefficient 3×10^{-7} per degree C. greater than the cladding, the cladding will be put into a state of compression, thereby strengthening the resultant fibre. For this combination of core and cladding glasses the softening point temperature for the core and cladding is 1485°C and 1310°C, respectively, values which are obtained from Figure 5. This mismatch of 175°C in the softening temperatures of the core and cladding glasses creates problems in

the fibre drawing process. Since the core glass has a higher softening point temperature than the cladding glass, the hole in the redraw blank cannot be closed. To prevent this problem the core should have a softening point temperature that is lower than that of the cladding to such an extent that the core viscosity is about 1-4 times lower than the cladding at drawing temperature.

A prior art technique for lowering the softening point temperature of the core involved adding B_2O_3 to the core glass. Addition of B_2O_3 does not, however, increase the refractive index of the core glass but increases the thermal expansion coefficient. To match this increased thermal expansion coefficient of the core glass, more B_2O_3 must be added to the cladding glass, thereby bringing back the viscosity mismatch problem. To overcome this problem of viscosity mismatch a core glass additive is needed which can increase the refractive index and decrease the viscosity without resulting in an increase in the thermal expansion coefficient.

In accordance with the present invention P_2O_5 is substituted for a portion of the GeO_2 in the core to lower the softening point temperature of the core without lowering the core refractive index. At the 0-30 wt.% dopant level the change in refractive index of SiO_2 due to GeO_2 and P_2O_5 is substantially linear and is about the same for both of these dopants. Thus, if P_2O_5 is substituted for some of the GeO_2 in the present example, the refractive index of the resultant glass is substantially unaffected, provided that the SiO_2 content remains unchanged. There is therefore a 23 wt.% ($\text{GeO}_2 + \text{P}_2\text{O}_5$), 77 wt.% SiO_2 glass which has substantially the same refractive index and substantially the same expansion coefficient as 23 wt.% GeO_2 , 77 wt.% SiO_2 glass. If Figure 5 is used in conjunction with equation 4 to select a ternary core glass having an acceptable softening point temperature, a trial and error approach may have to be used. For example, a core glass having the composition 5 wt.% P_2O_5 , 18 wt.% GeO_2 , 77 wt.% SiO_2 may be initially assumed. Referring to curve 64 of Figure 5, the softening point temperature of the binary glass 5 wt.% P_2O_5 , 95 wt.% SiO_2 is 1430°C. Since the assumed core glass contains 18 wt.% GeO_2 , the term yS of equation 4 is equal to (18×4.52) or 81.36°C. The softening point temperature of the assumed ternary glass, as determined by equation 4, is therefore 1348.64°C. Since the assumed core glass has a softening point temperature that is about 38°C greater than that of the cladding, it is unsatisfactory.

Since a core glass is needed having a greater amount of P_2O_5 than was present in the initially assumed composition, a core composition 10 wt.% P_2O_5 , 13 wt.% GeO_2 , 77 wt.% SiO_2 might be satisfactory. Again em-

playing equation 4 in conjunction with curve 64 of Figure 5, the softening point temperature is determined to be 1262°C. For this core composition the softening point temperature of the core is about 48°C. lower than that of the cladding, a relationship which is desirable in that it would enable the hole in the redraw blank to be more easily closed during fibre drawing.

Since the core and cladding glasses of optical waveguide fibres must be extremely pure, the core glass having a cation impurity level not exceeding ten parts per million, the fibres of the present invention should be produced by the flame hydrolysis process. After the core and cladding compositions are determined by some suitable method such as that described hereinabove, the various parameters of the flame hydrolysis apparatus such as temperature and flow rates of the constituents supplied to the flame are determined in a manner well-known to those skilled in the art. Due to the volatility of GeO_2 and P_2O_5 , an amount of these oxides less than the theoretically calculated amount is actually deposited. Thus the flow rates of the carrier gases through the liquid constituents which form these oxides must be empirically determined. The following examples illustrate the manner in which waveguides of different types and compositions are formed.

Example 1.

A specific example of forming an optical waveguide of the present invention is as follows. A blank containing core and cladding layers is prepared by a method similar to that disclosed in the aforementioned U.S.A. Patent No. 3,737,292. Germanium tetrachloride, GeCl_4 , vapours at a temperature of 32°C and silicon tetrachloride, SiCl_4 , vapours at a temperature of 32°C are fed to a flame hydrolysis burner by means of a dry oxygen-carrier gas at flow rates of 0.4 litre per minute and 2.0 litres per minute, respectively. Phosphorus trichloride, PCl_3 , vapours at a temperature of 35°C are carried to the flame hydrolysis burner by nitrogen flowing at a rate of 0.5 litre per minute. Natural gas and oxygen are fed to the burner at flow rates of 8 and 8.5 litres per minute, respectively. Glass soot from the flame hydrolysis burner is then deposited on a borosilicate glass starting rod having a 1/4 inch diameter. The starting rod is rotated at about 60 RPM and is translated with respect to the burner at a rate of about 1 inch per second. The soot is deposited on the starting rod until a diameter of about 1.5 inch is reached, the soot thus deposited constituting the fibre core. Gas flow through the GeCl_4 and PCl_3 is stopped, and a flow of BCl_3 is introduced into the burner at a rate of 0.28 litre per minute along with the continued flow of SiCl_4 vapour. The resultant B_2O_3 - SiO_2 soot, which will

constitute the fibre cladding, is deposited until the diameter of the soot blank is about 2.5 inches. The soot blank is then cooled and the starting rod is removed from the soot blank by sliding the starting rod out of the soot blank. The soot blank is then consolidated or sintered at a temperature of about 1350°C in a helium atmosphere. After the soot is consolidated, the blank has a diameter of about 1 inch and a length of about 4.5 inches. The blank is then heated to a temperature of about 1600°C and drawn in an oxygen atmosphere to the final optical waveguide dimensions.

An optical waveguide produced in accordance with the above example was drawn to an outside diameter of 125 μm , the cladding thickness being about 50 μm . The waveguide thus produced had a numerical aperture of 0.155 and an optical loss of 9.6 dB/km at a wavelength of 820 nm. The glass composition of the core was estimated to be 5 wt.% P_2O_5 , 6 wt.% GeO_2 and 89 wt.% SiO_2 , and that of the cladding was found to be 5 wt.% B_2O_3 and 95 wt.% SiO_2 .

Example 2.

A soot blank containing core and cladding layers is formed in accordance with a method similar to that described in Example 1, except that the core contains no silica. Oxygen is bubbled through POCl_3 and GeCl_4 , which are maintained at 35°C. and 32°C., respectively, to produce vapours which flow at 5.5 litre per minute and 1.0 litre per minute, respectively, to the burner. After a soot diameter of 1.5 inch has been built up on the 1.4 inch starting rod the core material gas flow stops and a flow of gases is initiated for forming the cladding material. Oxygen is bubbled through SiCl_4 , that is maintained at 32°C. and the resultant vapour is transported to the flame hydrolysis burner along with BCl_3 from a source which is maintained at 30°C. The flow rates of the oxygen through the SiCl_4 and BCl_3 vapours are 2.0 litres per minute and 0.73 litres per minute, respectively. After the diameter of the soot blank reaches 2.5 inches, it is cooled, and the starting member is removed. The soot blank is sintered at a temperature of about 550°C. in a helium atmosphere, and the resultant redraw blank is thereafter heated to about 650°C and drawn in an oxygen atmosphere to form a fibre. The composition of the core is 50 wt.% P_2O_5 and 50 wt.% GeO_2 , the cladding being 50 wt.% SiO_2 and 50 wt.% B_2O_3 . The NA of the resultant fibre is 0.77 which is greater than the value which can be obtained by forming a fibre core of either 100% GeO_2 or 100% P_2O_5 .

Example 3.

In a process similar to that described in Example 1 first and second layers of soot are deposited on a 1/4 inch diameter starting rod. The soot forming constituents are POCl_3 ,

GeCl₄, SiCl₄ and BCl₃ which are maintained at 35°C., 32°C., 32°C., and 25°C., respectively. To form the first soot layer, oxygen is bubbled through the POCl₃, GeCl₄ and SiCl₄ at rates of 3.1 litres per minute, 0.3 litre per minute and 1.0 litre per minute, respectively, and the resultant vapours are fed to the flame hydrolysis flame. When the diameter of the first soot coating reaches 1.5 inch, the gas flow through the POCl₃ and GeCl₄ is stopped, the rate of oxygen flow through the SiCl₄ is increased to 2 litres per minute, and BCl₃ is fed to the flame at a rate of 0.3 litre per minute. Soot deposition is continued until a diameter of about 2.5 inches is achieved. The soot blank is cooled, and the starting rod is removed. The soot blank is sintered at about 1000°C in a helium atmosphere to form a redraw blank that is drawn at a temperature of about 1150°C in an oxygen atmosphere to form a fibre having a numerical aperture of about 0.307. The composition of the core is 12 wt. % GeO₂, 22 wt. % P₂O₅ and 66 wt. % SiO₂, and that of the cladding is 20 wt. % B₂O₃ and 80 wt. % SiO₂.

One of the advantages of the present invention arises from the fact that most glass compositions in the ternary P₂O₅-GeO₂-SiO₂ system have refractive indices that are greater than those of the corresponding glasses of the binary GeO₂-SiO₂ system wherein the SiO₂ content is the same. This advantage can be illustrated by comparing the fibre of the last described example with similar fibres having germania silicate glass cores. The total dopant level (P₂O₅ + GeO₂) of the core of the fibre of Example 3 is 34 weight percent of the total glass composition. A fibre having a core consisting of 34 weight percent GeO₂ and 66 weight percent SiO₂ would have a numerical aperture of only 0.297, which is 0.01 less than that of the fibre of Example 3. If germania were the only dopant added to the silica to form a fibre core, 36 weight percent GeO₂ would be needed to provide a numerical aperture of 0.307, assuming that the cladding composition remained unchanged.

Example 4.

The following specific example of a waveguide of the present invention is one having a gradient index of refraction. Liquid GeCl₄ is maintained at a temperature of 32°C. in a first container, liquid SiCl₄ is maintained at 32°C in a second container, and liquid POCl₃ is maintained at 35°C. in a third container. Dry oxygen is bubbled through these liquid constituents so that vapours of each are picked up thereby and delivered to the burner. The oxygen is initially bubbled through the POCl₃, GeCl₄ and SiCl₄ at 3.1 litres per minute, 0.3 litres per minute and 2 litres per minute, respectively. Under these conditions the vapours entrained with the oxygen are hydrolyzed and oxidized within the flame of the flame hydro-

lysis burner to provide a soot of 22 wt. percent P₂O₅, 12 wt. per cent GeO₂ and 66 wt. percent SiO₂. The soot is deposited as a layer on a rotating and translating borosilicate glass tube having an outside diameter of 6 mm. As the soot layer builds up, the flow of dry oxygen through the GeCl₄ and POCl₃ liquids is continuously decreased to yield a soot layer of radially decreasing GeO₂ and P₂O₅ content. The reduction in oxygen flow through the GeCl₄ and POCl₃ is obtained by means of a cam profile being selected to produce the desired ultimate composition gradient. Control means such as that disclosed in U.S.A. Patent No. 3,826,560 is employed to vary the flow of liquid constituents. A composite structure 6 inches long and 1.5 inch in diameter and having a radially varying composition is deposited in about 2 hours. This soot will form the core of the resultant optical waveguide and has an axial refractive index of 1.49 measured at 589.3 nm. As the outside portion of the first soot layer is reached, the flow rate of gas through the POCl₃ and GeCl₄ is ceased, and a 0.3 litre per minute flow of BCl₃ is supplied to the flame hydrolysis flame. The initial 2 litre per minute flow of oxygen through the liquid SiCl₄ is continued. A layer of soot consisting of 20 wt. per cent B₂O₃ and 80 wt. percent SiO₂ is then deposited on the first soot layer. After consolidation, this second soot layer forms a layer of cladding glass having a refractive index of about 1.458. When the diameter of the blank reaches about 2.5 inches, the flow of all gases and vapors are stopped and the soot blank thus formed is cooled to room temperature. The starting rod is removed from the blank which is then sintered in a furnace having a helium atmosphere at about 1000°C. The resultant redraw blank is placed in an induction furnace and is drawn in an oxygen atmosphere at about 1150°C. As the structure is drawn, it decreases in diameter, and the central hole collapses. Drawing is continued until the final desired waveguide dimensions are obtained. An optical waveguide of this example may be drawn to an outside diameter of 5 mils.

WHAT WE CLAIM IS:—

1. An optical fibre comprising a cladding layer formed of high purity glass, and a core of high purity glass containing an amount of P₂O₅ and GeO₂ to provide a refractive index greater than that of said cladding layer, said core glass having a cation impurity level not exceeding 10 parts per million of transition elements.
2. A fibre as claimed in claim 1 wherein said core essentially consists of P₂O₅ and GeO₂.
3. A fibre as claimed in claim 1 wherein said cladding layer contains an amount of B₂O₃ such that the expansion coefficient of said cladding layer is less than that of said



GeCl₄, SiCl₄ and BCl₃ which are maintained at 35°C., 32°C., 32°C., and 25°C., respectively. To form the first soot layer, oxygen is bubbled through the POCl₃, GeCl₄ and SiCl₄ at rates of 3.1 litres per minute, 0.3 litre per minute and 1.0 litre per minute, respectively, and the resultant vapours are fed to the flame hydrolysis flame. When the diameter of the first soot coating reaches 1.5 inch, the gas flow through the POCl₃ and GeCl₄ is stopped, the rate of oxygen flow through the SiCl₄ is increased to 2 litres per minute, and BCl₃ is fed to the flame at a rate of 0.3 litre per minute. Soot deposition is continued until a diameter of about 2.5 inches is achieved. The soot blank is cooled, and the starting rod is removed. The soot blank is sintered at about 1000°C in a helium atmosphere to form a redraw blank that is drawn at a temperature of about 1150°C in an oxygen atmosphere to form a fibre having a numerical aperture of about 0.307. The composition of the core is 12 wt.% GeO₂, 22 wt.% P₂O₅ and 66 wt.% SiO₂, and that of the cladding is 20 wt.% B₂O₃ and 80 wt.% SiO₂.

One of the advantages of the present invention arises from the fact that most glass compositions in the ternary P₂O₅-GeO₂-SiO₂ system have refractive indices that are greater than those of the corresponding glasses of the binary GeO₂-SiO₂ system wherein the SiO₂ content is the same. This advantage can be illustrated by comparing the fibre of the last described example with similar fibres having germania silicate glass cores. The total dopant level (P₂O₅ + GeO₂) of the core of the fibre of Example 3 is 34 weight percent of the total glass composition. A fibre having a core consisting of 34 weight percent GeO₂ and 66 weight percent SiO₂ would have a numerical aperture of only 0.297, which is 0.01 less than that of the fibre of Example 3. If germania were the only dopant added to the silica to form a fibre core, 36 weight percent GeO₂ would be needed to provide a numerical aperture of 0.307, assuming that the cladding composition remained unchanged.

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lysis burner to provide a soot of 22 wt. percent P₂O₅, 12 wt. per cent GeO₂ and 66 wt. percent SiO₂. The soot is deposited as a layer on a rotating and translating borosilicate glass tube having an outside diameter of 6 mm. As the soot layer builds up, the flow of dry oxygen through the GeCl₄ and POCl₃ liquids is continuously decreased to yield a soot layer of radially decreasing GeO₂ and P₂O₅ content. The reduction in oxygen flow through the GeCl₄ and POCl₃ is obtained by means of a cam profile being selected to produce the desired ultimate composition gradient. Control means such as that disclosed in U.S.A. Patent No. 3,826,560 is employed to vary the flow of liquid constituents. A composite structure 6 inches long and 1.5 inch in diameter and having a radially varying composition is deposited in about 2 hours. This soot will form the core of the resultant optical waveguide and has an axial refractive index of 1.49 measured at 589.3 nm. As the outside portion of the first soot layer is reached, the flow rate of gas through the POCl₃ and GeCl₄ is ceased, and a 0.3 litre per minute flow of BCl₃ is supplied to the flame hydrolysis flame. The initial 2 litre per minute flow of oxygen through the liquid SiCl₄ is continued. A layer of soot consisting of 20 wt. per cent B₂O₃ and 80 wt. percent SiO₂ is then deposited on the first soot layer. After consolidation, this second soot layer forms a layer of cladding glass having a refractive index of about 1.458. When the diameter of the blank reaches about 2.5 inches, the flow of all gases and vapors are stopped and the soot blank thus formed is cooled to room temperature. The starting rod is removed from the blank which is then sintered in a furnace having a helium atmosphere at about 1000°C. The resultant redraw blank is placed in an induction furnace and is drawn in an oxygen atmosphere at about 1150°C. As the structure is drawn, it decreases in diameter, and the central hole collapses. Drawing is continued until the final desired waveguide dimensions are obtained. An optical waveguide of this example may be drawn to an outside diameter of 5 mils.

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2. A fibre as claimed in claim 1 wherein said core essentially consists of P₂O₅ and GeO₂.

3. A fibre as claimed in claim 1 wherein said cladding layer contains an amount of B₂O₃ such that the expansion coefficient of said cladding layer is less than that of said

core by an amount between 0 and 3×10^{-7} per °C.

- 5 4. A fibre as claimed in claim 3 wherein the softening temperature of said core glass is less than that of said cladding layer by up to about 50°C.

5. A fibre as claimed in claim 1 wherein said core has a gradient refractive index.

- 10 6. A fibre as claimed in claim 1 wherein said core has a substantially constant refractive index.

- 15 7. A fibre as claimed in claim 1 wherein said core glass comprises P_2O_5 , GeO_2 and SiO_2 and said cladding glass layer comprises B_2O_3 and SiO_2 , said core containing an amount of P_2O_5 that is sufficient to reduce the softening temperature of said core glass to a value which is less than that of said cladding glass by an amount between 0 and 50°C, and said cladding layer having an amount of B_2O_3 that is sufficient to increase the expansion coefficient of said cladding layer to a value greater than that of said core glass by

an amount between 0 and 3×10^{-7} per °C.

- 25 8. A fibre as claimed in claim 1 wherein the amount of P_2O_5 present in said core glass is 40—60 wt.% of the total amount of P_2O_5 and GeO_2 present therein.

30 9. A fibre as claimed in claim 1 having a light attenuation of less than 100 dB/km at wavelengths between 800 nm and 900 nm.

10. A fibre as claimed in claim 1 having a light attenuation of less than 10 dB/km at wavelengths between 800 nm and 900 nm.

- 35 11. An optical fibre substantially as described with reference to the accompanying drawings.

40 12. A method of making an optical fibre substantially as described with reference to the accompanying drawings.

ELKINGTON & FIFE,
Chartered Patent Agents,
High Holborn House, 52/54 High Holborn,
London, WC1V 6SH.
Agents for the Applicants.

