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(54) IMPROVEMENTS IN OR RELATING TO THE
MANUFACTURE OF INSULATING GLASS FIBRE SHEATHS

(71) We, COMMISSARIAT A L'ENERGIE ATOMIQUE, an organisation created in France by Ordinance No. 45-2563 of 18th October 1945, of 29 Rue de la Fédération, Paris 15e, France, 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:

The invention relates to a method of manufacturing an electrically insulating braided sheath of glass fibres, a device for carrying out the method and an insulated sheath obtained by the method.

More specifically, the invention relates to the manufacture of an insulating braided sheath comprising a braided sheath of glass fibres coated with a polymerized, cross-linked composition the insulating composition adhering firmly to each glass fibre in the sheath.

In conventional methods of obtaining a sheath of this kind, a braided sheath of glass fibres is coated with a composition which comprises polymerised substances in solution in a volatile solvent and which can be hardened by evaporating the solvent.

These processes do not give adequate productivity, since considerable time is required for processing a glass fibre braid. They also cause pollution since the evaporated solvent is discharged into the atmosphere.

In another known process, an article is coated with a composition which comprises polymerisable substances and which can be hardened by polymerizing the substances under the action of radiation.

In the case of the last-mentioned proces-

ses, it is known that the radiation characteristics and the operating conditions depend inter alia on the composition used. Some compositions can be hardened in the presence of air under the action of ultraviolet radiation.

However, the previously-mentioned processes, which use compositions which can harden in the presence of air under the action of ultraviolet radiation, are unsuitable for manufacturing an insulating braided sheath of glass fibres which has satisfactory mechanical properties such as resistance to bending. The reason for this is that the compositions used in these processes are not suited for coating a glass fibre braid since they do not provide sufficient adhesion between the composition and the glass fibres to give good mechanical properties to the insulating sheath.

The invention is concerned with a method of manufacturing an insulated braided sheath of glass fibres wherein a glass fibre braided sheath is coated with an insulating composition which hardens under the action of ultraviolet radiation in air and firmly adheres to the braided fibres.

The method according to the invention is characterised in that a braided sheath of glass fibres is impregnated and coated with a composition comprising at least one monounsaturated acrylic monomer, at least one polyunsaturated acrylic monomer, a photoinitiator and an organic peroxide, and the impregnated and coated sheath is irradiated with ultraviolet radiation in the presence of air.

This method has the advantage of yielding sheaths which are flexible, insulating, strong and resistant to temperature, since, when

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the braided sheath is coated, the composition ensures that the fibres have good wettability and, after polymerization and cross-linking under the action of ultra-violet radiation, adheres firmly to the braided fibres.

According to a preferred feature of the invention, the monounsaturated and polyunsaturated acrylic monomers in the composition for coating and impregnating the glass fibre braid are acrylic acid esters.

The monounsaturated acrylic acid esters, which are chosen so that their surface tension is suitable for obtaining good wettability of the braided fibres, are preferably butyl acrylate, isobutyl acrylate, or ethylene glycol monoacrylate.

The polyunsaturated esters of acrylic acid, which cause the composition to cross-link and are therefore chosen in dependence on the required mechanical properties of the sheath, are preferably ethylene glycol diacrylate, polyethylene glycol diacrylate, tetraethylene glycol diacrylate or pentaerythritol tetraacrylate.

According to another preferred feature of the invention, the proportion by weight between the monounsaturated and polyunsaturated monomers in the composition is between 1/3 and 2/1, since these proportions ensure a satisfactory rate of polymerization and cross-linking of the composition under the action of ultraviolet radiation, allowing for the time during which the braid of coated glass fibres is irradiated.

The photoinitiator, which is preferably added in a proportion by weight of between 1 and 5% to the mixture of monomers in the composition, is adapted to absorb the energy of the ultraviolet radiation photons and transmit it to the mixture in order to start the polymerization and cross-linking reaction.

The photoinitiator can be benzoin methyl ether or naphthalene sulphochloride.

The organic peroxide, which is preferably added in a proportion by weight between 1 and 10% to the mixture of acrylic monomers in the composition, is adapted to polymerise the composition all through the braid of glass fibres. Preferably the organic peroxide is benzoyl peroxide.

According to a further preferred feature of the invention, the composition also comprises a saturated epoxy resin which does not play any active part in polymerizing and cross-linking the composition, but can regulate the flexibility of the insulating sheath.

If a commercial epoxy resin is added to the mixture of monounsaturated and polyunsaturated acrylic monomers in a proportion by weight between 10 and 30%, the composition has a satisfactory polymerization and cross-linking rate, allowing for the time during which the coated braid is

irradiated.

A composition according to the invention comprising a saturated epoxy resin may comprise a vinyl monomer in addition to the said acrylic monomer, so as to increase the reactivity of the composition and obtain high processing speeds.

According to the invention, the vinyl monomer is preferably vinyl pyrrolidone or a monomer of a similar kind, e.g. 2 vinyl pyridine, 4 vinyl pyridine or 2 vinyl 5 ethyl pyridine.

A composition according to the invention, comprising a saturated epoxy resin and, if required, a vinyl monomer, may also comprise various additives such as a liquid elastomer, so as to increase the flexibility.

According to another preferred feature of the invention, the composition also comprises an epoxy resin which is unsaturated with acrylic acid and preferably has a double bond coefficient between 0.10 and 0.40 and an epoxy coefficient between either 0.48 and 0.57 or 0.19 and 0.22. The epoxy coefficient, of course, is the number of terminal epoxy groups per 100 g resin.

An unsaturated resin of this kind, if added to the mixture of acrylic monomers in a proportion by weight between 25 and 40%, ensures that the composition has a satisfactory polymerization rate when the impregnated and coated sheath is irradiated for a given time.

In the method according to the invention the irradiation time which, as we shall see, is defined by the speed with which the impregnated and coated sheath moves in front of the source of radiation, depends on the power of the source, e.g. a mercury vapour lamp.

The invention also relates to a device for carrying out the method according to the invention.

The device for carrying out the method of the invention comprises, in the path of a braided sheath of glass fibres, a set of means adapted to coat the sheath with a layer of the composition having a given thickness, while ensuring that the composition penetrates between the fibres of the sheath, the device also comprising an irradiation device, and is characterised in that the irradiation device comprises a tube emitting ultraviolet radiation, disposed inside and parallel to a cooled elliptical reflector, and a hemicylindrical mirror cooled by a flow of water, the concavities of the reflector and of the mirror, which are disposed on opposite sides of the path of the braided sheath and parallel thereto, being oriented towards one another.

The advantage of the device is that the braided sheath, after being coated, can be uniformly irradiated by a single ultraviolet emitter tube whilst the sheath travels only

once in front of the tube. This is because the rays emitted by the tube are reflected on a mirror, preferably of stainless steel, which is suitably disposed with respect to the tube, the reflector and the sheath, so that the sheath can be completely and uniformly irradiated when it moves in front of a single ultraviolet emitter tube.

We shall now give some non-limitative examples of the method according to the invention.

The examples, (1 to 11) were obtained by means of the device according to the invention, which is shown diagrammatically and by way of example in Figures 1 and 2 of the accompanying drawings. Each example corresponds to a given formulation of the braid-coating composition.

In the accompanying drawings:

Figure 1 diagrammatically shows the entire device for obtaining an insulated braided sheath according to the invention, and

Figure 2 is a diagram of a preferred embodiment of the device for irradiating the sheath.

As can be seen from the accompanying *Figure 1*, the device according to the invention comprises the following in succession, disposed on the path of a braided sheath of glass fibres 1 guided from a tape unit 3 by pulleys such as 5:

A vessel 7 disposed in the path of sheath 1 so that the sheath can be immersed in composition 8 in vessel 7 in order uniformly to coat the entire sheath 1,

A cup, dish or the like 9 having an inner recess 11 through which sheath 1 can pass, the inlet 12 of recess 11 being associated with a ball 13 which is previously introduced inside sheath 1 and which has a diameter greater than that of recess 7, so that the composition 8 can penetrate between the fibres of sheath 1,

A vessel 15 likewise containing a suitable quantity of composition 8 for coating sheath 1, the vessel being disposed in the path of the sheath in the same manner as vessel 7,

A second cup or the like 17 having a recess 19 through which sheath 1 can travel, recess 19 having a diameter such as to regulate the thickness of composition 8 with which sheath 1 is coated, and

An irradiation device 21.

According to the main feature of the invention, device 21, comprises, on opposite sides of the path of braided sheath 1, a tube 23 emitting ultraviolet rays and disposed inside an elliptical reflector 25, cooled, e.g. by a flow of air parallel thereto, and a hemicylindrical mirror 27 cooled by a flow of water 29.

Figure 2, by way of illustration, shows a preferred embodiment of a device 21 in which the components bear the same refer-

ence numbers as in *Figure 1*.

As can be seen from *Figure 2*, the emitter tube 23 is disposed at the focus 31 of a reflector 25. The reflector can be such that the distance between the foci 31, 33 of the corresponding ellipse can be between 54 and 89 mm.

The emitter 23 thus disposed inside reflector 25 is placed 122 mm from the coated glass fibre sheath 1.

When the emitter 23 and the reflector 25 are placed in this manner with respect to sheath 1, the hemicylindrical mirror 27, which has a diameter of 80 mm, is disposed so that sheath 1 is 20 mm from the centre 35 of mirror 27 situated on the axis extending through sheath 1 and tube 23.

Figure 2 also shows the path P_A of the photons emitted by tube 23 in the case of a reflector whose corresponding ellipse has a focus 33 at A, i.e. 64 mm from focus 31. *Figure 2* also shows the path P_B of the photons emitted by the tube 23 in the case of a reflector whose corresponding ellipse has a focus 33 at B, i.e. 89 mm from focus 31.

As can be seen, the irradiation device 21 in *Figure 2* can uniformly irradiate all the coated braid 1. Of course, braid 1 could similarly be uniformly irradiated by any device similar to that in *Figure 2*, but on a different scale.

Thus, in each of the examples 1 - 11 in which the previously described device is used, the glass fibre sheath 1 is coated and then continuously irradiated.

Sheath 1 is coated with composition 8 in the two vessels 7, 15 in two steps.

When sheath 1 enters vessel 7 and member 9, it is first coated with composition 8, which is driven between the fibres of the sheath. Next, when the sheath enters vessel 15 and member 17, it is coated a second time with composition 8, the thickness of the deposited composition being adjusted.

In each example, the sheath is moved at a speed of 20 m per minute and the ultraviolet emitter tube is a Hanovia (Registered Trade Mark) type mercury vapour lamp having a power of 80 W per linear cm of tube.

In each example 1 - 11, which corresponds to a given formulation of the composition 8 for coating sheath 1, the finished sheath is given an electric-voltage and a temperature test.

In the electric voltage test, the breakdown voltage of the sheath is evaluated when the sheath is disposed between two copper electrodes between which a voltage is applied, varying between 500 and 5 000 V. This test can be performed before or after the mechanical test, in which the processed sheath is rolled and unrolled in adjacent turns around a metal rod having a diameter equal to the internal diameter of the sheath.

The temperature test consists in placing the insulating sheath in an oven, the temperature of which is raised to 155°C.

Note that in all the following examples, the sheaths do not run after 5 consecutive days of testing.

Example 1

The composition used for coating a glass fibre braided sheath 1 had the following formulation:

90% of a mixture comprising 1/3 isobutyl acrylate and 2/3 polyethylene glycol diacrylate;

5% benzoin methyl ether; and
5% benzoyl peroxide.

The glass fibre sheath coated with this composition, after being dried under ultraviolet radiation, had a breakdown voltage of above 5 000 V before the mechanical test and 4 000 V after the mechanical test.

A sheath coated with this composition is very flexible.

Example 2

The composition used to coat a glass fibre braided sheath had the following formulation:

85% of a mixture comprising 1/3 butyl acrylate, 1/3 polyethylene glycol diacrylate and 1/3 of an epoxy resin modified with acrylic acid having a double bond coefficient of 0.35;

5% benzoin methyl ether; and
10% benzoyl peroxide.

The sheath coated with this composition, after drying, had a breakdown voltage of 5 000 V before the mechanical test and between 2 500 and 3 000 V after the mechanical test.

Example 3

The composition for coating a glass fibre braided sheath had the following formulation:

85% of a mixture comprising 1/3 ethylene glycol monoacrylate, 1/3 polyethylene glycol diacrylate and 1/3 epoxy resin modified with acrylic acid having a double bond index of 0.35; and

5% benzoin methyl ether and 10% benzoyl peroxide.

A sheath coated with this composition, after drying, had a breakdown voltage of 5 000 V before the mechanical test and between 2 500 and 3 000 V after the mechanical test.

Example 4

The composition for coating the glass fibre braided sheath had the following formulation:

90% of a mixture comprising 1/6 isobutyl acrylate, 1/2 ethylene glycol diacrylate and 2/6 of epoxy resin modified with acrylic acid

having a double bond coefficient of 0.35; 5% benzoin methyl ether; and 5% benzoyl peroxide.

A glass fibre braided sheath coated with this composition had a breakdown voltage of 5 000 V before the mechanical test and between 2 500 and 3 000 V after the mechanical test.

Example 5

The glass fibre braided sheath coating composition was as follows:

90% of a mixture comprising 1/6 butyl acrylate, 1/2 tetraethylene glycol diacrylate, and 2/6 of epoxy resin modified with acrylic acid having a double bond coefficient of 0.24;

5% benzoin methyl ether and
5% benzoyl peroxide.

A sheath of glass fibres coated with this composition had a breakdown voltage of above 5 000 V before the mechanical test and between 2 000 and 2 500 V after the mechanical test.

Example 6

The composition for coating the glass fibre braided sheath was as follows:

90% of a mixture comprising 1/9 butyl acrylate, 3/9 polyethylene glycol diacrylate, and 5/9 epoxy resin modified with acrylic acid having a double bond coefficient of 0.24;

5% benzoin methyl ether; and
5% benzoyl peroxide.

A glass fibre sheath coated with this composition had a breakdown voltage of 4 000 V after the mechanical test.

Example 7

The composition for coating the braided sheath 1 of glass fibre was as follows:

90% of a mixture comprising 2/10 ethylene glycol monoacrylate, 5.5/10 ethylene glycol diacrylate and polyethylene glycol diacrylate and 1.5/10 commercial saturated epoxy resin having an epoxy coefficient of 0.55;

5% benzoin methyl ether; and
5% benzoyl peroxide.

The glass fibre sheath coated with this composition had a breakdown voltage of 4 000 V after the mechanical test. Consequently a braid coated with this composition has high flexibility.

Example 8

The composition for coating the glass fibre braided sheath was as follows:

90% of a mixture comprising 4.1/10 of a mixture of ethylene glycol diacrylate and polyethylene glycol diacrylate, 2.35/10 ethylene glycol monoacrylate, 1.2/10 isobutyl acrylate and 2.35/10 commercial saturated epoxy resin having an epoxy coefficient of 0.55;

5% benzoin methyl ether; and
5% benzoyl peroxide.

70	75	80	85	90	95	100	105	110	115	120	125	130
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cient of 0.55;

5% benzoin methyl ether, and
5% benzoyl peroxide.

5 A glass fibre braided sheath coated with this composition had a breakdown voltage of above 5 000 V before the mechanical test and between 3 500 and 4 000 V after the mechanical test. A sheath coated with this composition has high flexibility.

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Example 9

The composition for coating the braided sheath of glass fibres was as follows:

15 90% of a mixture comprising 3/10 polyethylene glycol diacrylate, 1.75/10 vinyl pyrrolidone, 1.75/10 isobutyl acrylate and 3.5/10 of a commercial saturated epoxy resin having an epoxy coefficient of 0.21;

20 5% benzoin ethyl ether, and
5% benzoyl peroxide.

25 A fibre glass sheath coated with this composition had a breakdown voltage above 5 000 V before the mechanical test and between 3 000 and 3 500 V after the mechanical test.

Example 10

The composition for coating the glass fibre braided sheath was as follows:

30 90% of a mixture comprising 2.5/10 polyethylene glycol diacrylate, 1.5/10 vinyl pyrrolidone, 1.5/10 isobutyl acrylate, 3/10 of a commercial saturated epoxy resin having an epoxy coefficient of 0.21 and 1.5/10 of a commercial saturated liquid elastomer;

35 5% benzoin methyl ether, and
5% benzoyl peroxide.

40 A sheath of glass fibres coated with this composition had a breakdown voltage above 5 000 V before the mechanical test and between 3 000 and 3 500 V after the mechanical test. A braid coated with this composition has very high flexibility.

Example 11

The composition for coating the braided sheath of glass fibres was as follows:

50 90% of a mixture comprising 2.5/10 polyethylene glycol diacrylate, 1.5/10 vinyl pyrrolidone, 2.5/10 isobutyl acrylate and 3.5/10 of a mixture of 2 commercial saturated epoxy resins having an epoxy coefficient of 0.55 and 0.21 respectively;

55 5% benzoin methyl ether and
5% benzoyl peroxide.

60 A sheath of glass fibres coated with this composition had a breakdown voltage of above 5 000 V before the mechanical test and between 3 500 and 4 000 V after the mechanical test. A sheath coated with this composition has very high flexibility and very good resistance to high temperatures near 190°C.

WHAT WE CLAIM IS:

65 1. A method of manufacturing an elec-

trically insulating glass fibre sheath, characterised in that a braided sheath of glass fibres is impregnated and coated with a composition comprising at least one monounsaturated acrylic monomer, at least one polyunsaturated acrylic monomer, a photoinitiator and an organic peroxide, and the impregnated and coated sheath is irradiated with ultraviolet radiation in the presence of air.

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2. A method according to claim 1, characterised in that the acrylic monomers are selected from esters of acrylic acid.

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3. A method according to claim 1 or 2, characterised in that the monounsaturated monomer is chosen from the group comprising butyl acrylate, isobutyl acrylate, and ethylene glycol monoacrylate.

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4. A method according to claim 1 or 2, characterised in that the polyunsaturated monomer is chosen from the group comprising ethylene glycol diacrylate, polyethylene glycol diacrylate, tetraethylene glycol diacrylate and pentaerythritol tetraacrylate.

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5. A method according to any of claims 1 to 4, characterised in that the proportion by weight of the monounsaturated monomer to the polyunsaturated monomer is between 1/3 and 2/1.

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6. A method according to claim 1, characterised in that the photoinitiator is benzoin methyl ether.

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7. A method according to claim 1, characterised in that the photoinitiator is naphthalene sulphochloride.

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8. A method according to any of claims 1, 6 or 7, characterised in that the proportion by weight of the photoinitiator to the monomers is between 1 and 5%.

9. A method according to claim 1, characterised in that the organic peroxide is benzoyl peroxide.

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10. A method according to claim 1 or 9, characterised in that the proportion by weight of the peroxide to the monomers is between 1 and 10%.

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11. A method according to any of claims 1 to 10, characterised in that the composition also comprises an unsaturated epoxy resin.

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12. A method according to claim 11, characterised in that the epoxy resin has a double bond coefficient between 0.10 and 0.40.

13. A method according to claim 11 or 12, characterised in that the resin has an epoxy coefficient between 0.48 and 0.57.

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14. A method according to claim 11 or 12, characterised in that the resin has an epoxy coefficient between 0.19 and 0.22.

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15. A method according to any of claims 11 to 14, characterised in that the proportion by weight of the resin to the monomers is between 25 and 40%.

16. A method according to any of claims

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1 to 10, characterised in that the composition also contains a saturated epoxy resin.

17. A method according to claim 16, characterised in that the proportion by weight of the resin to the monomer is between 10 and 30%.

18. A method according to claim 16 or 17, characterised in that the composition comprises a vinyl monomer in addition to the said acrylic monomer.

19. A method according to claim 18, characterised in that the vinyl monomer is chosen from the group comprising vinyl pyrrolidone, 2 vinyl pyridine, 4 vinylpyridine, and 2 vinyl 5 ethyl pyridine.

20. A method according to any of claims 16 to 19, characterised in that the composition also comprises a liquid elastomer.

21. A method according to any of claims 11 to 20, characterised in that the proportion by weight of the photoinitiator to the mixture of monomers and epoxy resin is between 1 and 5%.

22. A method according to any of claims 11 to 20, characterised in that the proportion by weight of the organic peroxide to the mixture of monomers and epoxy resin is between 1 and 10%.

23. A device for carrying out the method according to any of claims 1 to 22, comprising, on the path of a braided sheath of glass fibres, a set of means adapted to coat the sheath with a layer of the composition having a given thickness, while ensuring that the composition penetrates between the fibres of the sheath, the device also comprising an irradiation device, characterised in that the irradiation device comprises a tube emitting ultraviolet radiation, disposed inside and parallel to a cooled elliptical reflector, and a hemicylindrical mirror cooled by a flow of water, the concavities of the reflector and of the mirror, which are disposed on opposite sides of the path of the braided sheath and parallel thereto, being oriented towards one another.

24. An insulating braided sheath of glass fibres obtained by the method according to any one of claims 1 to 22.

25. A method of manufacturing an electrically insulating glass fibre sheath as claimed in claim 1 substantially as hereinbefore described.

26. A device for use in the manufacture of an electrically insulated glass fibre sheath, constructed, arranged and adapted to operate substantially as described with reference to, and as shown in, the accompanying drawings.

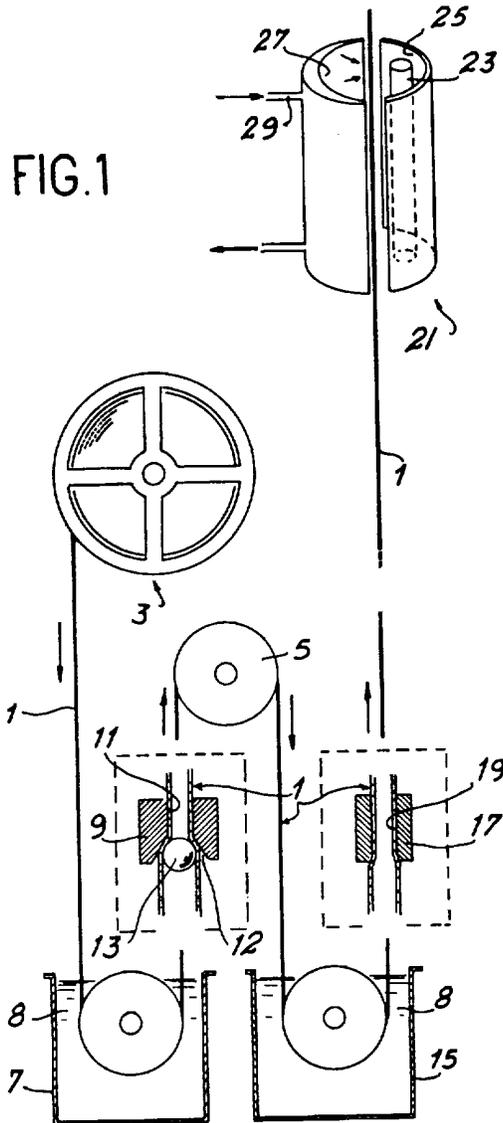
27. A insulating braided sheath of glass fibres as claimed in claim 24 substantially as hereinbefore described.

28. An insulating braided sheath of glass fibres which is substantially as described herein as a specific embodiment of the

sheath defined in claim 24.

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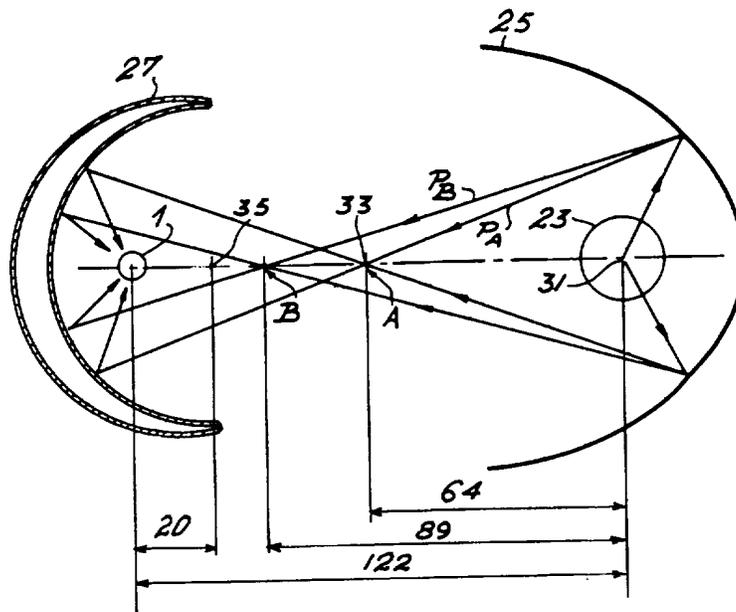


FIG. 2