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JP 110302509 A **US 5322660 A**

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(54) Abstract Title: **Fire resisting composition**

(57) A composition suitable for use in a fire resisting glazing product, comprises of an epoxy resin and a flame retardant; and the composition comprises by weight: 20-60% epoxy resin, such as epoxy novolac; 20-30% acid anhydride, such as methyl tetrahydrophthalic anhydride, methyl hexahydrophthalic anhydride, dodecenylsuccinic anhydride, nadic methyl anhydride; 15-20% phosphorous based flame retardant; 1-2 %coupling agent, such as alkoxysilane and 3-10% reactive diluent, such as 1,4-butane diglycidyl ether, 1,6-hexane diglycidyl ether. A method of making a fire resisting glazing product including an epoxy resin and a flame retardant is also disclosed.

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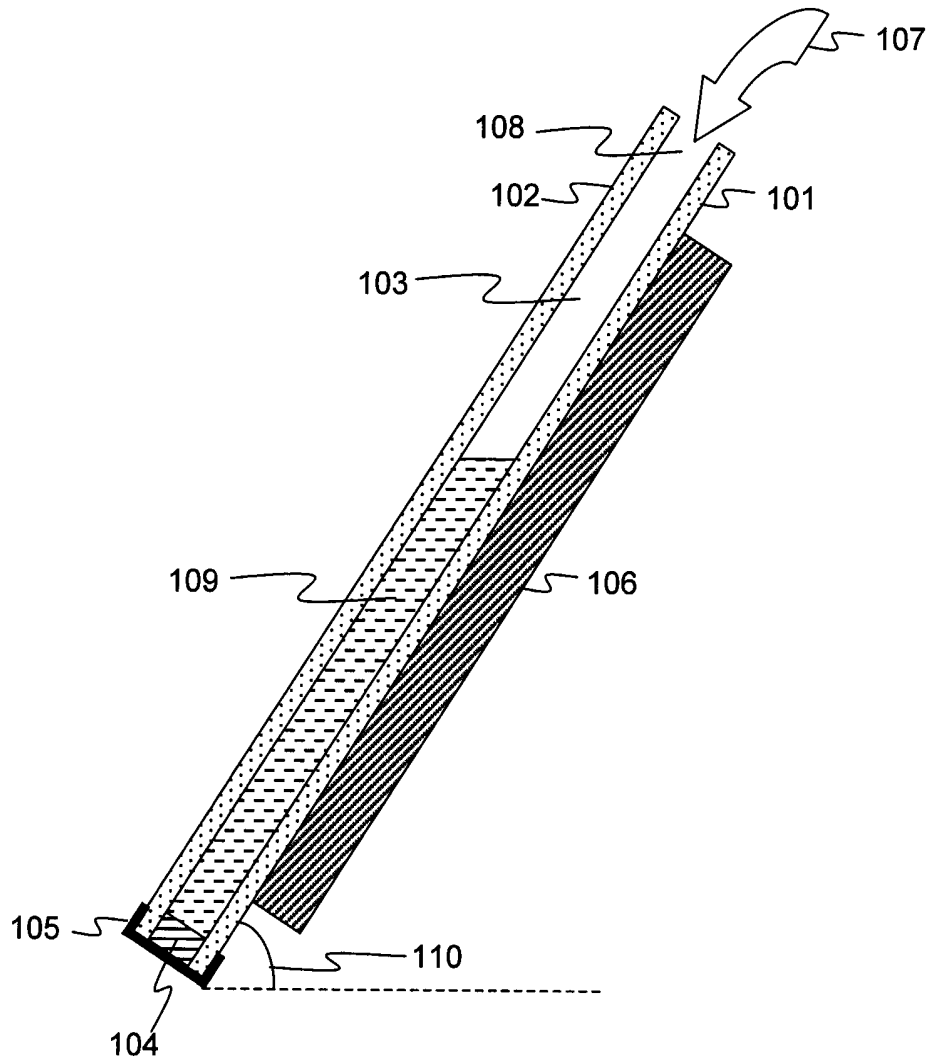


Fig. 1

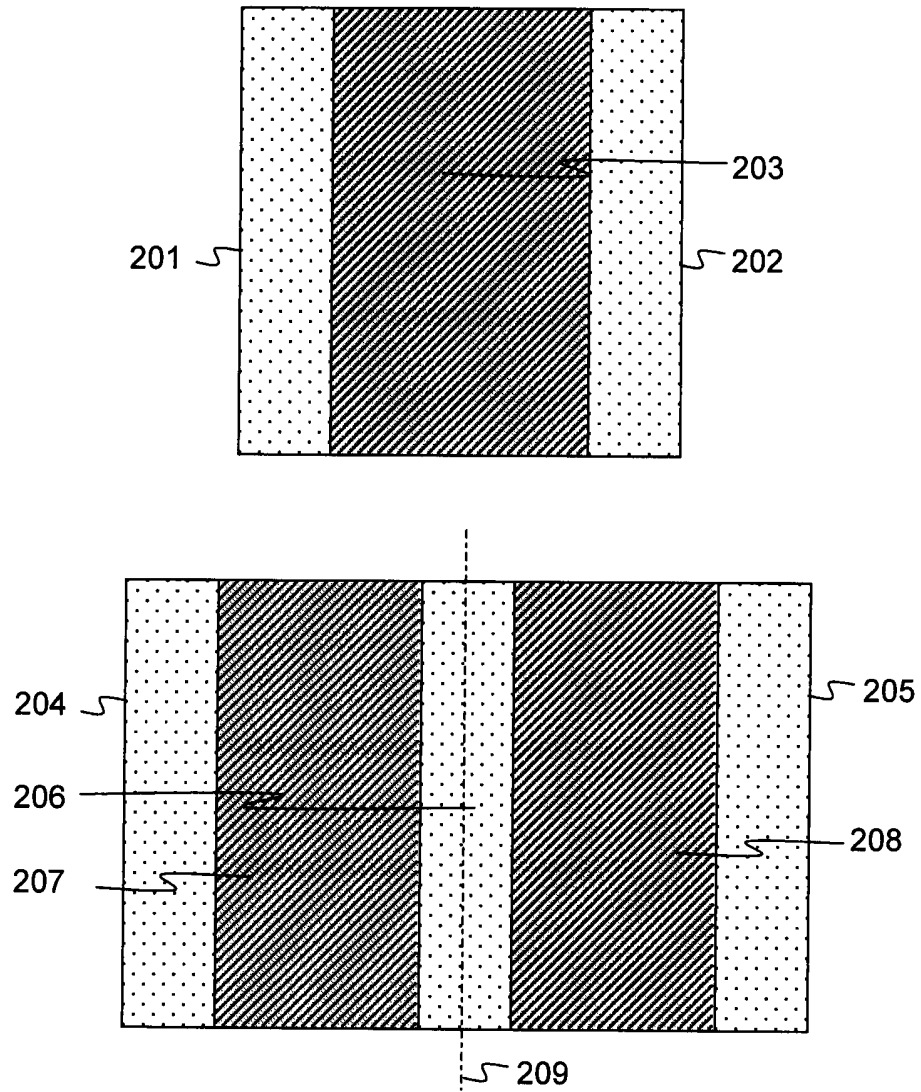


Fig. 2

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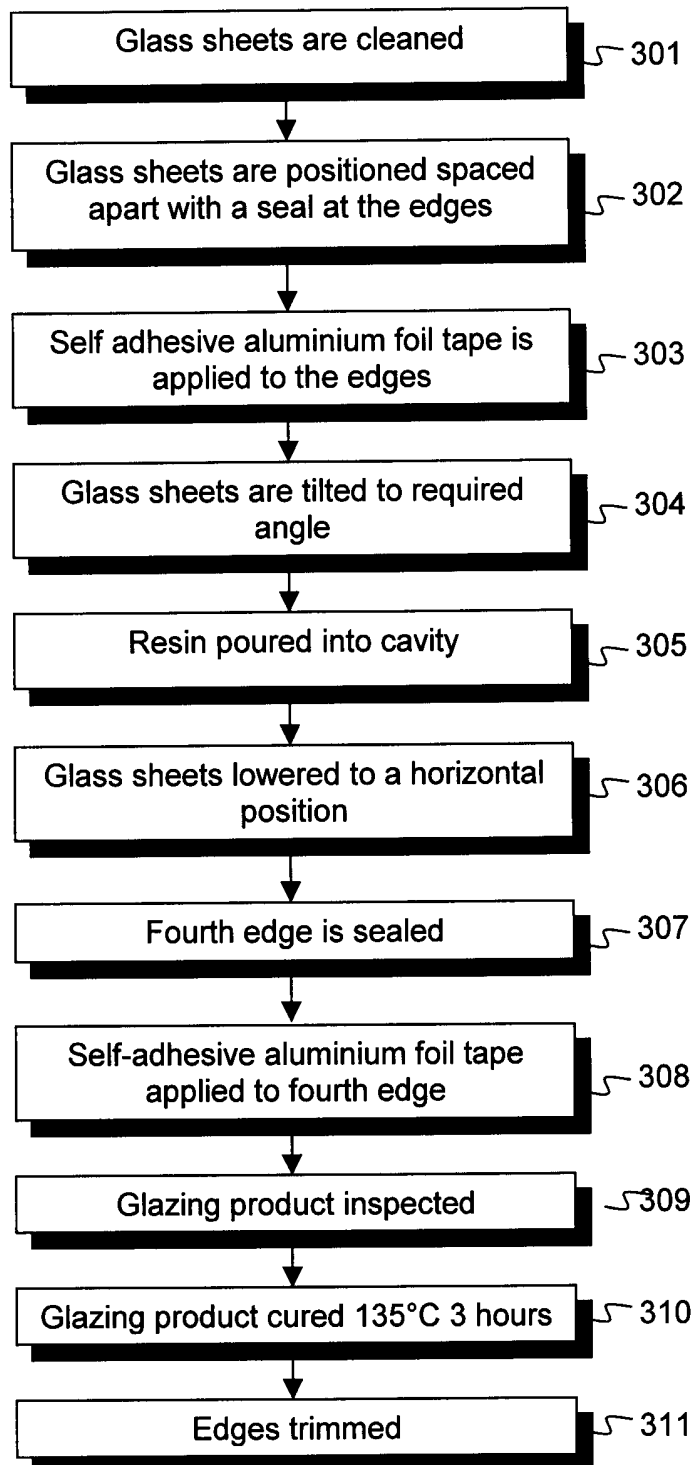


Fig. 3

FIRE RESISTING COMPOSITION

Field of the Invention

The invention relates to the field of fire resisting compositions for a
5 laminated fire resisting glazing product.

Background to the Invention

Annealed float glass has been produced for many years. However its
safety characteristics with respect to fire resistance as required by British,
10 European and World standards are insufficient. There are several methods of
upgrading annealed float glass to satisfy British, European and World safety
standards; these include tempering, incorporating a PVB layer between two glass
panels, applying a plastic film or adding a second glass panel and introducing a
plastics layer between the two glass panels and bonding them together. The
15 latter method tends to use liquid plastics materials.

Fire resisting test

According to European standard BS EN 1364-1: 1999 (superseding BS
476: Part 22: 1987) fire resisting tests for non-load bearing elements, which
20 includes fire resisting glass products, are classified in three ways. Letters are
used to classify three fire performance levels as 'E', 'W' and 'I'.

'E' = Integrity, and measures the ability of the glazing product to provide a
physical barrier against flame, hot gases and smoke.
25

'W' = Radiation, and measures the ability of the glazing product to reduce
the transmission of radiant heat through the glazing product below a specified
level e.g. 15 kW/m². This category is a requirement in only one or two EU
countries.
30

'I' = Insulation, and measures the ability of the glazing product to reduce
heat conduction through the glazing product to the non-fire side.

Integrity only and integrity, reduced radiation fire glass may be monolithic, thermally tempered glass, wired glass or a laminated glass/polymer glazing product. Currently all insulating fire glass types are multi-laminated in construction or contain a thick polymer interlayer.

Glass laminates

By glazing product, it is meant a laminate comprising at least two glass sheets spaced apart and at least one plastics material interlayer. The two glass sheets define a cavity between them, into which the interlayer of plastics material is introduced.

Methods of laminating annealed float glass panels together are well known. A known method is described in GB 2032844 in which reference is made to polyester resin, vinyl polymers and epoxy thermosetting resin as suitable materials for laminating glass panels together. GB 2032844 describes in detail a method of making laminates from frangible materials. Laminating bespoke glazing products together using liquid resin systems forming a safer glass is widely used. There are a number of glazing products, which use acrylic, silicon, UV cure polymers, methacrylate resin or polyester resins. The most popular systems are polyester thermosetting systems. Polyester resin systems provide efficient, low start-up cost and economical ways to bond two pieces of glass together. Polyester resins used in these systems have a low viscosity, which facilitates air release after mixing and offers good flow characteristics. A disadvantage is that they have a styrene content that necessitates good ventilation and adequate fire safety precautions.

Whilst the laminated glazing products described in GB 2032844 have adequate mechanical properties for strengthening, it has been found that they are inadequate for use in a laminated fire resisting glazing product. Although all of these materials can to some extent be modified with fire retardant additives to enhance their fire resistance for other commercial applications they are still

incapable of achieving results in line with standards for fire resisting glazing products when used between two glass panels as a laminated fire glass.

5 US 5,322,660 describes a glazing product manufactured using an epoxy based resin material, which details a production method of making a fire resisting laminated glazing product. In US 5,322,660, particular reference is made to heating the resin. Epoxy based resin materials have been found to give improved fire resistance when incorporated as in interlayer between spaced apart annealed glass sheets than some other systems used for fire resisting glazing products, 10 such as methacrylate resins. However, epoxy based liquid resin materials are usually too viscous at normal operating temperatures (25°C) to spread evenly when poured between two annealed glass sheets to form a fire resisting glazing product. The consequences of this high viscosity include the epoxy based resin material not spreading evenly between the two annealed glass sheets, and air 15 bubbles being introduced into the epoxy based resin material, which are not only unsightly for a transparent glazing product but are also deleterious to its fire resisting properties. US 5,322,660 describes that a simple reduction in viscosity of the epoxy based resin material by adding a diluent reduces the fire resisting properties of the glazing product, and increases the risk of air bubbles becoming 20 trapped in the epoxy based resin material. US 5,322,660 addresses this problem by describing a method of producing a fire resisting glazing product by introducing an epoxy based resin material into a cavity formed between two glass sheets *at an elevated temperature* and subsequently applying a force to the glass sheets to assist even spreading of the epoxy based resin material between those 25 two sheets. Elevated temperature of the resin is required to reduce viscosity, to enable other chemical elements to be added, to allow air-release to take place and to facilitate pouring between two glass panels.

30 US 5,322,660 also describes the need to raise the temperature of the annealed glass sandwich panels into which the resin is poured, to a temperature similar to that of the mixed resin material. This is to maintain the resin at the required temperature and therefore the required viscosity in order to assist the

flow of the resin in a cavity formed between the glass panels US 5,322,660 further describes, after pouring the liquid resin and forming a glazing product, a method of compressing the unit by using large heated plates in order to level the liquid resin material to make a glazing product of uniform thickness prior to heat curing. Heat curing is required to set the resin.

The use of elevated temperature described in US 5,322,660 has a further disadvantage in addition to requiring extra and more costly processing. The use of elevated temperature accelerates the curing time of the resin, reducing the effective working time of the liquid resin before it cures to a few minutes. In extreme cases, this could result in little or no air release being achieved during manufacture of a fire resisting glazing product.

US 5,322,660 further describes the thickness of the finished cured resin layer, for use as a wired fire resisting glass. A wired fire resisting glazing product comprises interleaving wires to improve the mechanical strength and stability of the glazing product. The thickness of the glazing product is described as no more than 3 mm e.g. 1.2 mm. However, for a glazing product without wires a thickness of up to 12 mm or so is indicated. A disadvantage of this method includes the many processes involved to achieve a laminated panel of glass. Furthermore, to produce a unit without wires a very thick resin layer is necessary, which adds considerable cost and leads to optical distortions.

Summary of the Invention

The inventor has realised the problems associated with the prior art, and devised a blend of materials that has a viscosity suitable for pouring a fire-resisting resin between two panels of glass without the need to heat the resin system or the glass panels prior to casting. The resulting fire-resisting glazing product provides a stable transparent non-wired laminated fire glass comprising a resin layer that forms an effective fire barrier.

According to a first aspect, there is provided a fire resisting composition for use in a fire resisting glazing product comprising by weight:

5	epoxy resin:	20.0-60.0%
	acid anhydride	20.0-30.0%
	phosphorous based flame retardant:	15.0-20.0%
10	coupling agent:	1.0-2.0%
	reactive diluent:	3.0-10.0%

Preferably, the fire resisting composition comprises 0.5 to 1.0% by weight
15 accelerator, the accelerator configured to reduce a cure time of the composition.

Preferably, the accelerator comprises a tertiary amine selected from the following:

20 benzyldimethylamine;

tris dimethyl amino-methyl phenol

Alternatively, the accelerator comprises an imidazole.

25 Preferably, the imidazole comprises 2-ethyl, 4-methyl-imidazole.

Preferably, the fire resisting composition further comprises 0.5 to 5.0% by weight of an ultraviolet light absorber.

30 Preferably, the ultraviolet light absorber comprises a compound selected from the following group:

benzotriazole;

benzophenone;

5

triazine.

Alternatively, the fire resisting composition further comprises 0.5 to 5.0% by weight of an ultraviolet light stabiliser.

10

Preferably, the ultraviolet light stabiliser comprises a compound selected from the following group:

hindered amine;

15

hindered phenol;

hindered benzoate.

20

Preferably, the fire resisting composition further comprises 5.0 to 10% by weight halogen flame retardant.

Preferably, the halogen flame retardant comprises a bromine-based compound.

25

Preferably the epoxy resin comprises epoxy novolac.

Preferably, the reactive diluent is selected from the following group:

30

1, 4-butane diglycidyl ether;

1, 6-hexane diglycidyl ether.

Preferably, the coupling agent comprises an alkoxysilane.

Preferably, the acid anhydride is selected from the following:

5

methyl tetrahydrophthalic anhydride;

methyl hexahydrophthalic anhydride;

10

dodecenylsuccinic anhydride (DDSA);

nadic methyl anhydride.

Preferably, the fire resisting composition comprises by weight:

15

epoxy novolac: 41.0-43.0%

tertiary amine: 0.5-1.0%

20

acid anhydride 23.6-25.0%

phosphorous based flame retardant: 17.0-18.5%

bromine based flame retardant: 5.0-7.5%

25

coupling agent: 1.0-2.0%

reactive diluent: 4.7-6.5%

30

UV absorber: 1.0-3.0%

According to a second aspect, there is provided a composition for use in a fire resisting glazing product, the composition comprising an epoxy resin and a flame retardant; and

5 the composition having a viscosity of less than 400 centipoise at 25°C

Preferably the composition has a viscosity of around 350 centipoise at 25°C.

10 According to a third aspect there is provided a method of making a fire resisting glazing product comprising:

 spacing a first glass sheet and a second glass sheet apart such that the second glass sheet is disposed substantially parallel and opposing the first glass
15 sheet;

 sealing at least three edges of the glass sheets, such that the first glass sheet and the second glass sheet define a cavity therebetween;

20 introducing an epoxy based resin material comprising a fire retardant material into the cavity;

 curing the first glass sheet, the second glass sheet and the epoxy based resin material to form a laminated glazing product;

25 characterized in that the epoxy based resin material is introduced into the cavity at substantially room temperature.

 Preferably the first glass sheet and the second glass sheet are at
30 substantially room temperature.

Preferably the curing step comprises:

heating the first glass sheet, the second glass sheet and the epoxy based resin material for around 2 hours at around 135°C.

5 **Brief Description of the Drawings**

For a better understanding of the invention and to show how the same may be carried into effect, there will now be described by way of example only, specific embodiments, methods and processes according to the present invention with reference to the accompanying drawings in which:

10

Fig. 1 illustrates schematically a side elevation view of an epoxy based resin material being introduced between two spaced apart glass sheets.

15 Fig. 2 illustrates schematically a cross-section of glazing products having one or more epoxy resin based laminate layers.

Fig. 3 illustrates a flow diagram of a process for making laminated fire resisting glazing products.

20 **Detailed Description**

There will now be described by way of example a specific mode contemplated by the inventors. In the following description numerous specific details are set forth in order to provide a thorough understanding. It will be apparent however, to one skilled in the art, that the present invention may be
25 practiced without limitation to these specific details. In other instances, well known methods and structures have not been described in detail so as not to unnecessarily obscure the description.

30 A laminated glass panel is produced using a pair of annealed (ordinary) float glass sheets being spaced apart in parallel relationship, and sealed at their edges to form a cavity. A liquid thermosetting resin is introduced into the cavity

and subsequently cured to form a glass lamination providing fire resistance and safety characteristics.

Referring to Fig. 1 herein, there is illustrated schematically a side elevation
5 view of an epoxy based resin material being introduced between two spaced
apart glass sheets. There is provided a first glass sheet 101, a second glass
sheet 102, which have a cavity 103 between them. Each sheet has four edges.
Towards three of the four edges, a spacer 104 is placed to maintain the sheets
101, 102 in a substantially parallel relationship. A further adhesive seal 105 is
10 also provided on the outside of the three edges.

Annealed float glass is used for the first glass sheet 101 and the second
glass sheet 102, as it is commonly found in modern buildings and, as opposed to
drawn glass, is manufactured world-wide and is readily available from a large
15 number of glass merchants. The glass sheets 101, 102 can range in size from
as small as 50mm x 50mm too as large as 5.00m². Patterned, textured, tinted,
etched, brilliant-cut, painted, screen printed or otherwise processed glass, as fire
tested or assessed, can also be incorporated as one of the glass panels 101, 102
making up the fire resisting laminated unit. The glass sheets 101, 102 may be
20 from 2 mm to 19 mm thick. Whatever thickness is selected, both sheets of glass
101, 102 for a 3-ply fire resisting glazed product must be of a similar thickness.

By a 3-ply unit it is meant a unit comprising a first glass sheet 101, a layer of
resin, and a second glass sheet 102 such that the layer of resin is sandwiched
25 between the first glass sheet 101 and the second glass sheet 102. Fire resisting
glazing units having more than 3-ply construction can also be manufactured.
Referring to figure 2 herein, there is illustrated schematically a cross-section of
glazing products having one or more epoxy resin based laminate layers. In
Figure 2A there is illustrated a 3-ply fire resisting glazing product comprising a
30 first glass layer 201, a second glass layer 202, and a resin layer 203 sandwiched
between the first glass layer 201 and the second glass layer 202. In Figure 2B
there is illustrated a 5-ply fire resisting glazing product comprising a first glass

layer 204, a second glass layer 205 and a third glass layer 206. There is also provided a first resin layer 207 and a second resin layer 208. The first resin layer 207 is sandwiched between the first glass layer 204 and the third glass layer 206, and the second resin layer 208 is sandwiched between the second glass layer 205 and the third glass layer 206.

Whatever configuration of ply is used, the fabricated fire resisting glazing product should be symmetrical about a centre line 209 through the thickness of the product. This is to ensure that the product has the same fire resisting properties regardless of which side a fire is, and to ensure that if a fire is only expected on one side of a product (for example, the interior of a building), the fire resisting glazing product cannot be accidentally installed the wrong way round.

The spacer 104 the perimeter of the glazing product comprises double sided adhesive tape. The thickness of the tape determines the width of the cavity 103 between the first glass sheet 101 and the second glass sheet 102. A resin thickness of between 1 mm to 3 mm is preferred, and typically 1.1 mm is used. Suitable double sided adhesive tapes are manufactured from urethane foam, PVC foam, foamed acrylic and polyolefin foams. Foamed acrylic tapes are preferred as they offer good bonding to the glass sheets 101, 102 and display sufficient hardness to withstand the weight of the upper glass panel without compressing, which if compressed would result in reduced cavity 103 thickness. Foamed acrylic tapes also withstand the temperatures at which the fire resisting glazing product is exposed to during the elevated temperature curing process.

In addition to spacer 104, a further adhesive seal 105 comprising a self-adhesive aluminium foil tape is placed around the outside edges of the first glass sheet 101 and the second glass sheet 102. This further seals the edges of the glass sheets 101, 102 prior to heat curing, to act as a secondary seal in the event any small amount of resin material escapes before it is fully cured. The aluminium foil tape also offers protection to the edges of the glass and protection to operatives working with the glazing product.

An epoxy resin blend 109 is introduced 107 into the cavity 103 between the first glass sheet 101 and the second glass sheet. The epoxy resin blend comprises fire retardant materials. The epoxy resin blend 109 is introduced into the cavity 103 at the edge 108 where there is a gap in the spacer 104 such that epoxy resin blend can be poured into the cavity 103 and air can be released from the cavity 103.

Epoxy resin is a thermosetting resin and is known for good resistance to heat. Common types of base epoxy resin include, phenolic, novolac, bisphenol A, bisphenol F and bisphenol A/F mixture resins and these resins are used in composites, coatings, adhesives, encapsulation and electrical applications, civil and mechanical engineering products. The most widely used epoxy resin is a bisphenol A epoxy resin. Of all these epoxy resins phenolic and novolac resins are known to have higher resistance to heat. However, phenolic resins are dark in colour and therefore unsuitable for this application as transparency is required.

Epoxy novolac resin to be a suitable epoxy resin. Epoxy novolac resin in its base form is very viscous and chemical manufacturers may supply epoxy novolac resins already mixed with a reactive diluent to provide a less viscous more workable product. If necessary, a reactive diluent can be added to facilitate processing by providing a more pourable resin. There are a range of diluents available including mono-functional, di-functional and multi-functional displaying suitable characteristics. From this range typically a 1,4 – butane diglycidyl ether or 1,6 – hexane diglycidyl ether can be reacted with the novolac resin.

Thermosetting resin systems such as epoxy novolac resins require a curing agent or hardener to react with the resin in order to achieve a solid cured material. Epoxy novolac hardeners include aliphatic amines, amidoamines, polyamides, polyimides, polyetheramines, cycloaliphatic amines, aromatic amines, latent imidazole, acid anhydrides and latent catalytic agents.

A novolac resin, diluent and hardener mix has been found to be incapable of withstanding the extreme heat of a British or European Standard fire test. Additional modifications are therefore required to achieve a resin in a fire resisting glazing product to withstand the extremes of a fully developed fire. There are an abundance of fire retardant additives that provide assistance to polymer materials reaction to extreme heat. However, it has been found only a limited number of fire retardants are suitable for use in an application such as this where transparency is an important characteristic. Suitable fire retardant additives can have a phosphorus content, e.g. resorcinol bis diphenyl phosphate, bisphenol A bis diphenyl phosphate and isopropylated triphenyl phosphate. These compounds offer clear, low viscosity advantages. Other suitable fire retardant additives include phosphite additives, aryl or alkyl phosphite or a mix of both and diaryl or dialkyl hydrogen phosphites, suitably triphenyl phosphite, triisodecyl phosphite or a diphenyl phosphite, which displays a higher phosphorus content. Phosphite compounds also have the advantage of acting as a polymer stabiliser and under extreme heat exposure certain elements undergo a chemical change to form a sticky substance that adds stability to the fire resisting glazing unit.

It has been found that halogen fire retardant products are also helpful with achieving a good reaction against extreme heat and bromine materials are known to be more effective than chlorine materials. Most bromine based flame retardants are commercially available in powder form, although some are available in liquid form and it is preferred to use a liquid bromine based flame retardant. Liquid halogen based flame retardants can increase the viscosity of the blend.

The fire retardant products described above are not designed for the present invention, as placed between two or more glass panels, but rather for applications to prevent the surface spread of flame. Annealed float glass will not support the surface spread of flame. However annealed float glass will vent on exposure to rapid temperature rises and through those vents provide an avenue for oxygen supplies to the polymer material it surrounds fanning the combustion

process when exposed to high temperatures. A phosphorous-based flame retardant acts mostly by physical action in the condensed phase by providing a protective layer thereby reducing available oxygen and impeding the combustion process. Phosphorous based flame retardants also react in the solid phase by forming a carbon layer on the polymer surface.

A halogen flame retardant acts mainly in the gas phase by a chemical reaction to suppress the combustion process. The exothermic combustion process is slowed and the supply of flammable gases from the resin are reduced.

It has been found that phosphorous flame retardant materials and halogen flame retardant materials added to a novolac resin work well in providing resistance to extreme heat during the different stages of the combustion process the resin endures. It has also been found that the combination of phosphorous and halogen flame retardant materials utilised in this way gives greater stability to the novolac resin during pyrolysis and succeeds in providing support to the fire resisting glazing product during exposure to extreme heat. It has also been found that the resulting char formed on combustion of incorporated phosphorous and halogen flame retardant materials produces a solid charred layer which in effect supports the glass sheets 101, 102 in their fractured condition during exposure to extreme heat. Whilst it is preferred to use a combination of a halogen flame retardant and a phosphorous flame retardant, it is not essential that the blend includes a halogen flame retardant as adequate results can be achieved using only the phosphorous flame retardant. Under conditions of fire, the phosphorous flame retardant becomes sticky and assists in maintaining the mechanical stability of the glazing point up until the point where the phosphorous flame retardant begins to char.

Since epoxy resins have an aromatic structure they can be affected to some extent by ultraviolet (UV) light and in almost all situations for glazing products, this originates from the sun. The effect of UV light is to cause the transparent epoxy resin to lend the glazing product an undesirable yellow colour, or in extreme

cases to become opaque. This is detrimental to the appearance of the fire resisting glazing product. An ultraviolet light absorber is used to overcome the effects of ultraviolet light. There are a number of known ultraviolet light absorbing products suitable for inclusion into a novolac resin system and they include a
5 benzotriazole or benzophenone and a more recent addition known as triazine.

Recent advancements to polymer additives that resist the effects of sunlight exposure are hindered amine, hindered phenol and hindered benzoate light stabilisers, which act as free radical scavengers in the polymer system. These
10 additives are not ultraviolet light absorbers, but ultraviolet light stabilisers and for some compositions may be used in place of an ultraviolet light absorber.

The float glass on each side and an ultraviolet absorber or stabiliser within the resin system provide a stable laminated fire resisting glazing product. Many
15 ultraviolet absorbers are commercially available in powder form, and can be mixed with a reactive diluent before incorporating into the blend. Where transparency is not a requirement of the glazing product, an ultraviolet absorber is not required.

20 It is desirable to include a coupling agent to improve adhesion between the organic epoxy resin layer 109 and the glass sheets 101, 102. It is known that alkoxysilanes improves the ability of an epoxy resin to bond to a glass surface. It has been found that an alkoxysilane material offers additional adhesion of the resin system to the glass sheets 101, 102 of the present invention especially
25 when exposed to extreme heat. Alkoxysilanes can be included in the blend of materials making up the resin mix or they can be diluted and sprayed onto the inner surface of each glass sheet 101, 102 before assembly or it may be incorporated using a combination of both methods.

30 There is a range of epoxy novolac hardeners or curing agents that can be used giving a range of final cured resin characteristics. It is desirable to use a curing agent that will lead to a fire resisting glazing product that is capable of

withstanding extreme heat. Curing agents that can be used to fabricate a fire resisting glazing product include a latent/catalytic cure system or an anhydride/accelerator cure system.

5 Anhydride/accelerator cure systems include methyl tetrahydrophthalic anhydride, methyl hexahydrophthalic anhydride, dodecenylsuccinic anhydride (DDSA) and nadic methyl anhydride. The advantage of these materials is that they are slow reacting, which provides extended standing time for air release after mixing. Anhydride systems also have the advantage of providing long gel
10 times, which allow large batches at a time to be mixed for automated feed on larger production line facilities, as they will have a longer 'pot life', that is to say large quantities of the resin mix can be prepared beforehand and can be kept for some time before they must be used. Most other amine cure systems would not be practical in automated feed production lines as the gel times are too short and
15 hardened resin would choke feed lines and holding tanks.

 Standing times for the anhydride cure systems described above are typically 0.5 – 1 hour depending on the ambient temperature. A cure accelerator is used to shorten the elevated temperature cure time, that is to say the cure time
20 of the anhydride cure system if the temperature is raised above ambient. Suitable accelerators include tertiary amines (benzyl dimethylamine or tris dimethyl amino-methyl phenol) or an imidazoles such as 2-ethyl, 4-methyl-imidazole for the anhydride cure system. The use of a tertiary amine with the acid anhydride system allows a lower quantity of acid anhydride to be used to
25 achieve an adequate cure. It is advantageous to reduce the quantity of acid anhydride used in the mix, as it has been found that a resin containing a high ratio of acid anhydride/resin burns during a fire more freely than a resin containing a lower ratio of acid anhydride/resin. However, it is not essential that a tertiary amine is used as the acid anhydride may achieve an adequate cure given
30 a long enough time, high enough temperature or combination of time and temperature.

Curing the epoxy novolac system of the present invention is achieved by elevated temperature baking in an industrial box oven. An advantage of the present invention is that elevated temperature cycles of a low temperature for a short period then cooling followed by high temperature bake for several hours are unnecessary. It has been found cure rates for an anhydride/accelerator system would be a single cycle of 125°C – 150°C for 1 – 3 hours typically 135° for 2 hours. It has also been found that anhydride/accelerator cure systems offer a good glass transition temperature (a temperature measurement of when the cured resin begins to soften under heat conditions), good clarity and optimum characteristics when exposed to short elevated temperature baking.

Alternatively, the fire resisting glazing product can achieve similar fire resisting results substituting a latent/catalytic cure system for the anhydride/accelerator cure system. A similar elevated temperature cure programme cycle would be as described before. The disadvantage of the latent/catalytic types is the overall system is more expensive and has slightly less clarity than the anhydride/accelerator cure system. However, latent/catalytic cure systems offer good glass transition temperatures good clarity and good cured characteristics.

Example

Referring to Fig. 3 herein, there is illustrated a flow diagram of a process for making laminated fire resisting glazing products.

A first glass sheet 101 and a second glass sheet 102 of stock size glass of 3mm or 4mm thick measuring for example 2440mm wide x 1220mm high are prepared by first passing them through a glass washing machine 301. Modern machines also dry the glass before the process is finished and in many cases the machine capacity will determine the largest panel of glass that can be cleaned. Glass cleaning can also be achieved manually by use of a proprietary glass cleaner. A thorough visual inspection is carried out before the double-sided adhesive tape is applied.

The first glass sheet 101 is then placed on a horizontal and substantially flat glass table. Double-sided tape 104 is applied on all four sides at the edge of the glass sheet 101. Two small gaps are left at each end of the side, for final air release, in which the liquid resin will be introduced. A protective film or backing film is removed from the upper surface of three sides. The backing film to the fourth side, where the liquid resin is to be introduced, remains until all the liquid resin has been poured between the glass layers. The second clean glass panel is placed above the first and laid on top in a parallel position 302. A seal is formed around the perimeter of the glass sheets 101, 102 to prevent the liquid resin running out from between the glass layers.

Self adhesive aluminium foil tape 105 is then applied 303 forming a channel around three edges, which acts as an additional barrier to any small leaks of resin that may escape through the double-sided adhesive tape 104.

The first glass sheet 101 is supported on a support 106, which is then tilted 304 to a required angle 110 so as to elevate the fourth edge 108, where the backing film has remained. The position or angle 110 of elevation is to suit the flow of resin material to the bottom of the unit.

A measured amount of activated liquid resin material 109 using an anhydride/tertiary amine cure system is poured 305 into the cavity 103 between the first glass sheet 101 and the second glass sheet 102. Owing to the viscosity of the liquid resin material 109 and gravitational forces, the liquid resin flows to the bottom of the cavity 103. As the cavity 103 is filled the resin 109 moves towards the upper open edge 108. Air is evacuated through the top edge 108.

Final air release is achieved when the unit is lowered 306 to a horizontal position and the liquid resin 109 moves towards the unsealed fourth edge 108 of the unit. At this point the backing film is removed from the tape of the top fourth edge 108 and a seal is formed, apart from gaps left at each end. Final air

release occurs through these gaps which are sealed 307 with silicone or similar material to retain the liquid resin material between the glass sheets.

5 Self-adhesive aluminium foil tape is then applied 308 to this fourth and final edge. At this point an inspection is made 309 to ensure the glazing product is fully sealed, that there are no residual air bubbles and that there are no vents in the glass before it is moved to the oven for elevated temperature curing. If it is found the seal is inadequate further aluminium foil tape can be applied. Residual air at the perimeter of the glazing product is acceptable, and air bubbles trapped
10 further towards the centre of the glazing product may be moved by elevating the glazing product to allow the bubble to rise and terminate at the perimeter. Vents in the glazing product will normally render it unusable; it should be discarded in a safe and environmentally approved manner.

15 After pouring, final inspection and prior to elevated temperature curing, completed glazing products are stored on a suitable rack assembly for bulk cure. A suitable rack assembly allows circulation of hot air all around the glazing products whilst in the oven. It is essential to support and maintain the glazing product in a near horizontal position to prevent the liquid resin material bulking to
20 the lower side. A deviation of no more than 10° to the horizontal is acceptable for producing a uniform thickness of cured resin layer between the glass sheets 101, 102. When the required quantity of units have been fabricated the rack assembly is rolled into the industrial box oven. Single or multiple glazing products can be cured in this way however it is more economical to cure batch quantities at a
25 time.

The glazing product is cured 310 for 2 hours at 135°C . This allows the resin 109 to set and form a solid laminate with the first glass sheet 101 and the second glass sheet 102.

30

Once the glazing product has been cured, the edges can be trimmed 311 to remove edges where air remains and the adhesive tape 105 and spacer 104.

The blend of the resin is important, as it must have a sufficiently low viscosity at around room temperature to be adequately poured between the two glass sheets 101, 102. If the viscosity of the liquid resin is too high then the resin
5 may not pour adequately and air bubbles can become entrained in the fire resisting glazing product.

A blend of epoxy novolac resin, reactive diluent, phosphorous fire retardant, halogenated fire retardant, alkoxysilane, ultraviolet light stabiliser and curing
10 system of anhydride/tertiary amine provide a mix that has good clarity, low viscosity and a long pot life. This blend of materials provides a mix that will retain a low viscosity and in a stable condition for several days. It allows ample time for air release to take place and is easily suited for batch fabrication of laminated units. It has been found the low viscosity resin mix overcomes the need for a
15 press, to force the unit together making a uniformly thick resin layer, as the resin mix finds its flat level when placed horizontally on the flat glass table. It has also been found unnecessary to heat the epoxy novolac and additives to reduce its viscosity or to heat the glass to maintain a similar temperature to the resin. This is because the low viscosity epoxy novolac resin mix flows freely at room
20 temperature (around 25°C) and disperses between the glass sheets 101, 102. It has been found a working environment of temperatures between 10°C and 30°C provides a suitable atmosphere for the epoxy resin blend used.

A suitable blend has been found to be:

25

Epoxy Novolac	41.0-43.0% by weight
Reactive Diluent	4.7-6.5
Acid Anhydride	23.6-25.0
Phosphorus Flame Retardant	17.0-18.5
30 Bromine Flame Retardant	5.0-7.5
Coupling Agent	1.0-2.0
Tertiary Amine	0.5-1.0

UV Absorber 1.0-3.0

This blend can be heat cured at 130° – 140° C for 1.5-2.0 hours

5 It has been found that this blend has a viscosity as follows:

25°C 345 centipoise

26°C 278 centipoise

28°C 242 centipoise

10

This compares to viscosity at 25°C of the individual components of the blend as follows:

	Epoxy novolac resin:	30,000 - 50,000 centipoise
15	Acid anhydride:	45 - 65 centipoise
	Phosphorous flame retardant:	10 – 17 centipoise
	Halogen flame retardant:	1,800 centipoise
	Coupling agent:	3 centipoise
	Reactive diluent:	14 – 21 centipoise
20	Tertiary amine:	120 – 250 centipoise
	UV absorber:	introduced as a powder

25

This viscosity range is suitable for pouring the blend at room temperature.

30

Suitable space for a 'clean room', an environment that is maintained at temperatures between 10°C and 30°C and kept relatively dust free, is used for mixing materials and fabrication of the laminated glazing product. Automatic pumps and production line facilities can be set up if required. The glazing product manufacture has low start-up costs or it can be easily incorporated into

existing glass tempering production facilities. Glazing products of this type do not require expensive processing machines as production utilises equipment most medium and large glass companies already have. A further advantage of the current invention is that it utilises readily available glass panels or stock glass.

- 5 The glazing product can, for example, be fabricated during the latter hours of the working day allowing an elevated temperature cure overnight by a thermostatic timer on the industrial oven box. New stocks will be ready for cutting and shipping the next day.

- 10 According to a second specific embodiment, double glazed units are provided incorporating one or more leaves of the fire resisting glazed product, the other leaf being of clear annealed or tempered or otherwise processed as before described. The spacer bar utilised in double glazed units of the current invention must be that of a stainless steel type to provide the necessary support when
15 exposed to extreme heat.

According to a third specific embodiment, glazed units are provided in a bent curved section configuration.

- 20 The glazed products described herein, when manufactured in a 3-ply configuration, can provide fire resistance of 30 minutes expressed as EW30. Further, by increasing the number of laminations, e.g. 3 glass panels and 2 resin layers, fire resistance of E60 can be achieved.

- 25 Additionally, the glazed products of 3-ply or multiples thereof comply with the safety requirements of BS EN 12600 (superseding BS 6206: 1981) Impact Test as class 2B, which will allow the glazed products to be used in all applications as defined by e.g. UK Buildings Regulations Part N.

Claims:

1. A fire resisting composition for use in a fire resisting glazing product comprising by weight:

5	epoxy resin:	20.0-60.0%
	acid anhydride	20.0-30.0%
	phosphorous based flame retardant:	15.0-20.0%
10	coupling agent:	1.0-2.0%
	reactive diluent:	3.0-10.0%

15 2. A fire resisting composition for use in a fire resisting glazing product as claimed in claim 1 further comprising 0.5 to 1.0% by weight accelerator, said accelerator configured to reduce a cure time of said composition.

20 3. A fire resisting composition as claimed in claim 2 wherein said accelerator comprises a tertiary amine selected from the following:

benzyldimethylamine;

tris dimethyl amino-methyl phenol

25

4. A fire resisting composition as claimed in claim 2 wherein said accelerator comprises an imidazole.

30 5. A fire resisting composition as claimed in claim 4 wherein said imidazole comprises 2-ethyl, 4-methyl-imidazole.

6. A fire resisting composition for use in a fire resisting glazing product as claimed in any of claims 1 to 5 further comprising 0.5 to 5.0% by weight of an ultraviolet light absorber.

5 7. A fire resisting composition as claimed in claim 6 wherein said ultraviolet light absorber comprises a compound selected from the following group:

benzotriazole;

10

benzophenone;

triazine.

15 8. A fire resisting composition for use in a fire resisting glazing product as claimed in any of claims 1 to 5 further comprising 0.5 to 5.0% by weight of an ultraviolet light stabiliser.

9. A fire resisting composition as claimed in claim 8 wherein said
20 ultraviolet light stabiliser comprises a compound selected from the following group:

hindered amine;

25

hindered phenol;

hindered benzoate.

10. A fire resisting composition for use in a fire resisting glazing product
30 as claimed in any of claims 1 to 9 further comprising 5.0 to 10% by weight halogen flame retardant.

11. A fire resisting composition as claimed in any claim 10 wherein said halogen flame retardant comprises a bromine-based compound.

12. A fire resisting composition as claimed in any preceding claim
5 wherein said epoxy resin comprises epoxy novolac.

13. A fire resisting composition as claimed in any preceding claim wherein said reactive diluent is selected from the following group:

10 1, 4-butane diglycidyl ether;

1, 6-hexane diglycidyl ether.

14. A fire resisting composition as claimed in any preceding claim
15 wherein said coupling agent comprises an alkoxysilane.

15. A fire resisting composition as claimed in any preceding claim wherein said acid anhydride is selected from the following:

20 methyl tetrahydrophthalic anhydride;

methyl hexahydrophthalic anhydride;

dodecenylsuccinic anhydride (DDSA);

25

nadic methyl anhydride.

16. A fire resisting composition as claimed in claim 1 comprising by weight:

30

epoxy novolac: 41.0-43.0%

	tertiary amine:	0.5-1.0%
	acid anhydride	23.6-25.0%
5	phosphorous based flame retardant:	17.0-18.5%
	bromine based flame retardant:	5.0-7.5%
	coupling agent:	1.0-2.0%
10	reactive diluent:	4.7-6.5%
	UV absorber:	1.0-3.0%

15 17. A composition for use in a fire resisting glazing product, said composition comprising an epoxy resin and a flame retardant; and

 said composition having a viscosity of less than 400 centipoise at 25°C

20 18. A composition as claimed in claim 17 wherein said composition has a viscosity of around 350 centipoise at 25°C.

 19. A method of making a fire resisting glazing product comprising:

25 spacing a first glass sheet and a second glass sheet apart such that said second glass sheet is disposed substantially parallel and opposing said first glass sheet;

 sealing at least three edges of said glass sheets, such that said first glass
30 sheet and said second glass sheet define a cavity therebetween;

introducing an epoxy based resin material comprising a fire retardant material into said cavity;

5 curing said first glass sheet, said second glass sheet and said epoxy based resin material to form a laminated glazing product;

characterized in that said epoxy based resin material is introduced into said cavity at substantially room temperature.

10 20. A method of making a fire resisting glazing product as claimed in claim 19 wherein said first glass sheet and said second glass sheet are at substantially room temperature.

15 21. The method of making a fire resisting glazing product as claimed in claim 19 or claim 20 wherein said curing step comprises:

heating said first glass sheet, said second glass sheet and said epoxy based resin material for around 2 hours at around 135°C.

Amendments to the claims have been filed as follows

28

Claims:

1. A fire resisting composition for use in a fire resisting glazing product comprising by weight:

5 epoxy resin: 20.0-60.0%

acid anhydride 20.0-30.0%

1.0 phosphorous based flame retardant: 15.0-20.0%

coupling agent: 1.0-2.0%

reactive diluent: 3.0-10.0%

15 2. A fire resisting composition for use in a fire resisting glazing product as claimed in claim 1 further comprising 0.5 to 1.0% by weight accelerator, said accelerator configured to reduce a cure time of said composition.

20 3. A fire resisting composition as claimed in claim 2 wherein said accelerator comprises a tertiary amine selected from the following:

benzyl dimethylamine;

25 tris dimethyl amino-methyl phenol

4. A fire resisting composition as claimed in claim 2 wherein said accelerator comprises an imidazole.

30 5. A fire resisting composition as claimed in claim 4 wherein said imidazole comprises 2-ethyl, 4-methyl-imidazole.

11. A fire resisting composition as claimed in any claim 10 wherein said halogen flame retardant comprises a bromine-based compound.

12. A fire resisting composition as claimed in any preceding claim
5 wherein said epoxy resin comprises epoxy novolac.

13. A fire resisting composition as claimed in any preceding claim wherein said reactive diluent is selected from the following group:

10 1, 4-butane diglycidyl ether;

1, 6-hexane diglycidyl ether.

14. A fire resisting composition as claimed in any preceding claim
15 wherein said coupling agent comprises an alkoxysilane.

15. A fire resisting composition as claimed in any preceding claim wherein said acid anhydride is selected from the following:

20 methyl tetrahydrophthalic anhydride;

methyl hexahydrophthalic anhydride;

dodecenylsuccinic anhydride (DDSA);

25 nadic methyl anhydride.

16. A fire resisting composition as claimed in claim 1 comprising by weight:

30 epoxy novolac: 41.0-43.0%

	tertiary amine:	0.5-1.0%
	acid anhydride	23.6-25.0%
5	phosphorous based flame retardant:	17.0-18.5%
	bromine based flame retardant:	5.0-7.5%
	coupling agent:	1.0-2.0%
10	reactive diluent:	4.7-6.5%
	UV absorber:	1.0-3.0%

15 17. A composition for use in a fire resisting glazing product, said composition comprising an epoxy resin and a flame retardant; and

 said composition having a viscosity of less than 400 centipoise at 25°C

20 18. A composition as claimed in claim 17 wherein said composition has a viscosity of around 350 centipoise at 25°C.

 19. A method of making a fire resisting glazing product comprising:

25 spacing a first glass sheet and a second glass sheet apart such that said second glass sheet is disposed substantially parallel and opposing said first glass sheet;

 sealing at least three edges of said glass sheets, such that said first glass
30 sheet and said second glass sheet define a cavity therebetween;

introducing the composition as claimed in any of claims 1 to 18 into said cavity;

5 curing said first glass sheet, said second glass sheet and said epoxy based resin material to form a laminated glazing product;

characterized in that said composition is introduced into said cavity at substantially room temperature.

10 20. A method of making a fire resisting glazing product as claimed in claim 19 wherein said first glass sheet and said second glass sheet are at substantially room temperature.

15 21. The method of making a fire resisting glazing product as claimed in claim 19 or claim 20 wherein said curing step comprises:

heating said first glass sheet, said second glass sheet and said epoxy based resin material for around 2 hours at around 135°C.



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Application No: GB0507948.8

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Examiner: Dr Albert Mthupha

Claims searched: 1-18

Date of search: 30 August 2005

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
A	-	US5322660 A (MILLER CONSTRUCTION LTD), see column 7 lines 45-55, Example, Claims 1 & 14.
A	-	JP11302509 A (SHINKO ELEC.), see WPI Abstract AN 2000-033675 [03].

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^x :

C3V

Worldwide search of patent documents classified in the following areas of the IPC⁰⁷

B32B; C08G; C08K; C08L

The following online and other databases have been used in the preparation of this search report

ONLINE : EPODOC, WPI.