

PATENT SPECIFICATION

(11) 1 589 878

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- (21) Application No. 49416/76 (22) Filed 26 Nov. 1976
(23) Complete Specification Filed 24 Nov. 1977
(44) Complete Specification Published 20 May 1981
(51) INT. CL.³ B32B 17/00 25/14
(52) Index at Acceptance
B5N 1700 2514
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(54) A METHOD OF MANUFACTURING A HOLLOW PANEL

(71) We BFG GLASSGROUP, a Groupement d'Interet Economique, established under the laws of France (French Ordinance dated 23rd September 1967) of Rue de Teheran 7, F 75008 - Paris, 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:

This invention relates to a method of manufacturing a hollow panel by uniting vitreous sheets by means of a spacer of synthetic polymeric located between and adherent to margins of such sheets. The invention also relates to spacer materials for such panels.

Prior art methods in the category referred to are capable of use in the mass production of hollow glazing units but there is need for improvements in certain respects. It is often important to achieve a predetermined spacing of the vitreous sheets in the finished panel in a reproducible manner. This has proved to be difficult by some of the known methods due to characteristics of the prefabricated spacer strips, including minor variations in their cross-sectional dimension, and/or to problems associated with the assembly and jointing of the sheets and spacer strips. Another disadvantage, attributable to various of the known methods, is that the panels do not satisfy one or more quality specifications which panel do not satisfy one or more quality specifications which panel manufacturers are now frequently asked to observe and which relate specifically to properties of the spacer itself. The forces to which the spacers are subjected in course of use due to their manner of installation or environmental conditions require spacers to have a certain inherent strength but at the same-time a certain elasticity. Panels made by known methods have developed various faults which are attributable to the inter-sheet joints. Some of these faults are clearly due to inadequate mechanical properties of the spacers but others have proved to be more difficult to explain.

An object of the present invention is to provide a method by which vitreous sheets can be joined at a predetermined spacing, within very close tolerances. Another object is to provide such a method which is suitable for use under industrial conditions in the mass production manufacture of hollow panels with high quality hermetically sealed joints between the panel sheets such as may be required, for example, in hollow glazing units for installation in the exterior walls of buildings.

According to the present invention, there is provided a method of manufacturing a hollow panel by uniting vitreous sheets by means of a spacer of synthetic polymeric material located between and adherent to margins of such sheets, characterised in that a spacer with a tensile strength of at least 4 kg/cm², an elongation at break in excess of 50% and a water permeability of the polymeric material less than 0.2 g of water per m² of surface per 24 hours per mm of material thickness per cm of Hg pressure is formed in situ from a hardenable viscoelastic ribbon which has cross-sectional dimensions and a viscosity sufficient to maintain the two vitreous sheets at at least the required final intersheet spacing under the weight of the superimposed sheet when the sheets are disposed horizontally with the ribbon between them, the panel being formed by laying said ribbon upon the margin of one of the sheets, laying the other sheet in position, supported by the ribbon, and then subjecting said ribbon to hardening conditions to convert it into said spacer while the vitreous sheets are at said final required spacing.

This method can be economically applied on an industrial scale with reproducible results. One very important factor leading to this advantage is the formation of the spacer in situ

from a ribbon which is able to support the superimposed vitreous sheet. It is not necessary to employ any extraneous temporary means for maintaining the vitreous sheets at the required final spacing while the ribbon undergoes conversion to a spacer strip with the specified properties. The assembly of the panel components is very simple. The thickness of the ribbon (i.e. that dimension thereof which is measured normally to the vitreous sheet on which the ribbon is initially laid) is not critical in the sense that the thickness of a finished prefabricated spacer strip would be critical. The ribbon thickness can exceed the required spacing between the vitreous sheets in the finished panel because the ribbon can be easily permanently deformed to make its thickness equal to the required inter-sheet spacing before the strip is hardened.

Furthermore the method according to the invention yields panels with inter-sheet joints having a combination of properties which has been found to be important for good performance, which properties include a high degree of water impermeability of the sheet spacer. This factor contributes considerably to reducing deterioration of the inter-sheet joints during prolonged use of the panel.

The viscoelastic ribbon may be a continuous length of the viscoelastic material which is laid along the entire peripheral margin of the said one vitreous sheet. As an alternative the ribbon may comprise two or more separate lengths of such material which are laid along different margins of such sheet and which may be caused or allowed to become joined or bonded together end to end during or after that operation. The terms "ribbon" and "spacer" where used in the above definition of the invention are to be construed accordingly, i.e. to include not only a single piece ribbon and a single piece spacer respectively but also a ribbon and a spacer composed of separately fabricated lengths of material.

The term "hardening" where used in the above definition of the invention in relation to the viscoelastic ribbon is used as a compendious term to denote an increase in viscosity and strength due to change in chemical composition of the ribbon and the cognate term "hardenable" is to be construed accordingly. The chemical change may for example involve vulcanisation or chemical cross-linking.

In a preferred method according to the invention the viscoelastic ribbon is extruded onto the margin of the said one vitreous sheet. It is very convenient to carry out the invention in this way. Storage of viscoelastic ribbon awaiting use is obviated and the ribbon is applied in fresh condition.

The strip material can be extruded in a factory in which the seals or joints are formed and the quality of the extruded product can easily be checked and adjusted at any time.

The ribbon can be laid progressively along the margin of the vitreous sheet by extruding the ribbon onto that sheet while the extruder and the said sheet are relatively displaced.

As an alternative procedure the ribbon can be derived from a temporary storage facility. For example the extruded ribbon can be coiled preparatory to withdrawal from the coil to an assembly station. An anti-adhesive material, e.g. a material in powder form, may be applied to the extruded ribbon to prevent too firm adhesion between the convolutions.

In preferred methods according to the invention the thickness of the ribbon (measured in a direction normal to the vitreous sheets between which it is located preparatory to the hardening operation) is in excess of the said required final inter-sheet spacing and pressure is exerted on the assembly to bring the sheets to that required value before the ribbon is converted into the spacer. Preferably this is accomplished while the assembly is on a horizontal support, by means of one or more rollers spaced above that support by a distance equal to the required final intersheet spacing, the support and roller(s) being relatively displaced to cause the roller(s) to bear against the upper vitreous sheet.

The viscoelastic ribbon is preferably formed of a composition having at 80°C a viscosity of 40,000 to 120,000 poises estimated by means of a Brabender plastograph wherein a bladed rotor is rotated at 10 revolutions per minute in a quantity of the composition at 80°C held in a container. The resistance to rotation of the rotor is compared with the resistance to rotation in a reference material and the result is used as a basis for the estimated viscosity of the sample. As stated above the range of 40,000 to 120,000 is not critical. Compositions outside that range can be used, e.g. compositions having an viscosity up to 250,000 poises.

The viscoelastic ribbon must be capable of resisting significant deformation under the forces imposed by the superencumbent vitreous sheet and of resisting any permanent deformation under any forces which may be imposed by the handling of the ribbon, e.g. coiling and uncoiling as hereinbefore referred to, before it is laid on one of the vitreous sheets in the panel assembly operation.

Preferably the viscoelastic ribbon has a tensile strength of from 0.5 to 3 kg/cm². These values for the tensile strength of the viscoelastic ribbon and the values hereinafter given relating to the tensile strength of the spacer formed from the viscoelastic ribbon are obtained according to French Standard NF. 46.002 using an H3 type gauge and a traction

rate of 50 cm/minute.

In preferred embodiments of the invention the viscoelastic ribbon has an elongation at break in excess of 700%.

5 In certain embodiments of the invention the composition of the viscoelastic ribbon and the hardening conditions to which it is subjected are such that the spacer has a tensile strength of from 4 to 50 kg/cm². These values are not critical. For example the spacer may have a somewhat higher tensile strength. Generally speaking the best panels incorporate a spacer having a tensile strength of at least 10 kg/cm², the optimum range being 12 to 16 kg/cm². 5

10 Advantageously, the composition of the viscoelastic ribbon and the hardening conditions are such that the spacer has an elongation at break exceeding 100% e.g. between 150 and 500%, the optimum range being 150 to 450%. 10

15 Preferred categories of synthetic polymeric materials for forming the viscoelastic ribbon comprise curable elastomeric materials and particularly those which by appropriate selection of curing or vulcanising agents can be cured at relatively low temperatures, say less than 100°C. Deserving of particular mention are composition based on one or more butyl rubbers alone or in combination with other polymers such as ethylene/vinyl acetate copolymers or polyisobutylene, compositions based on one or more ethylene/propylene terpolymers particularly terpolymers of ethylene and propylene with a diene (e.g. dicyclopentadiene, hexadiene or a bornene such as 2-ethyl norbornene) such as 20 compositions based on a combination of an ethylene/propylene terpolymer and polyisobutylene, and compositions based on depolymerised butyl e.g. on a combination of such a polymer with an ethylene/vinylacetate copolymer with or without the addition of some other elastomer. 20

25 The foregoing is a summary of the most preferred elastomeric composition but it is of course within the scope of the invention to use a viscoelastic ribbon composition of another type. As other examples reference is made to extrudable compositions based on a butadiene/styrene copolymer or a butadiene/acrylonitrile copolymer, and to compositions based on chlorosulphonated polyethylene (e.g. a chlorosulphonated polyethylene as marketed under the Trade Mark "Hypalon" by DuPont de Nemours), or on reaction products of aliphatic dihalide compounds with metal polysulphides (polysulphide rubbers). 30

35 Curable viscoelastic ribbon compositions will include an appropriate cross-linking or vulcanisation agent. Vulcanising agents suitable for compositions based on butyl rubber and ethylene/propylene terpolymers include p.quinone dioxime in the presence of an oxidiser. Various halomethyl phenolic resins can be used for curing unsaturated elastomers at elevated temperatures or even at room temperature (ref. "Ambient Curing of Unsaturated Elastomers with Halomethyl Phenolic Resins" by Kenneth C. Petersen: Paper presented to the Division of Rubber Chemistry, American Chemical Society, April 1971). Peroxides are suitable for cross-linking ethylene/propylene terpolymers and agents for cross-linking such polymers at room temperature and based on hydroperoxides are described in a paper by L. Corbelli and S. Giovanardi entitled "Crosslinking of Ethylene-Propylene Terpolymers at Room Temperature" published in the report of the Montedison Petrochemical Division Research Centre (1975). 40

45 Preferably the viscoelastic ribbon is capable of being and is in fact cured at less than 100°C to form the spacer in situ. The selection of the viscoelastic composition so that curing can take place without the necessity for the ribbon to be heated to high temperatures of 100°C or more is of practical advantage for reducing manufacturing costs. The manufacture of the panels is particularly facilitated if curing can take place at ambient temperature or with only moderate heating. 45

50 If heating of the viscoelastic ribbon is required to bring about its conversion to a spacer with the required properties, this can be achieved by placing the panel assembly in an oven. Alternatively heating can be confined to the region of the assembly where the spacer is located. Localised heating can for example be effected by a high-frequency heating technique provided that a polar compound e.g. neoprene, is included in the ribbon composition or the composition includes a sufficiently high proportion of a suitable filler e.g. carbon black, or titanium, zinc or barium oxide. 55

In carrying out a method according to the invention it is often advantageous to pre-heat at least the margins of the vitreous sheets before applying the viscoelastic ribbon.

60 Preferably the viscoelastic ribbon incorporates a mixture of polymeric substances in substantially different molecular weight categories. The use of polymers in substantially different molecular weight categories in the formation of the ribbon composition is recommended because adjustment of the relative proportions of such substances affects the viscoelastic properties and by appropriate selection of these proportions the visco-elastic ribbon can be given a favourable combination of properties enabling it to be conveniently laid, to support the superimposed vitreous sheet and to form after conversion a spacer with 65

excellent mechanical properties which provide a stable and strong inter-sheet joint with adequate flexibility to withstand rupture due to flexure of the vitreous sheets e.g. due to thermal gradients across the panel or, in the case of exterior glazing units, to wind forces.

5 It is advantageous to employ a ribbon composition wherein there is a said mixture of
polymeric substances which comprises at least one curvable polymeric material and at least
one polymeric material in a substantially lower molecular weight category than such curvable
polymeric material(s) and wherein the weight ratio of the relatively low molecular weight
category polymeric material(s) to the relatively high molecular weight category polymeric
10 material(s) is between 0.5:1 and 1.6:1. According to another advantageous embodiment use
is made of a said mixture of polymeric substances wherein there is at least one curvable
polymeric material and at least one polymeric material in a substantially higher molecular
weight category than said curvable polymeric material(s) and wherein the weight ratio of the
relatively low molecular weight category polymeric material(s) to the relatively high
15 molecular weight polymeric material(s) is higher than 2.5:1.

By way of example the viscoelastic ribbon composition may comprise a low molecular
weight butyl rubber (m.w. between 5000 and 50,000) e.g. Butyl LM and a high molecular
weight butyl rubber (mw 400,000 to 600,000) e.g. Butyl B268, or a butyl rubber and a
polyisobutylene of substantially higher or lower molecular weight than the butyl rubber.

The invention includes methods wherein the composition of the viscoelastic ribbon is
20 based on one or more synthetic elastomers and is capable of being and is in fact applied in
heated condition and converted to form said spacer by cooling in situ, e.g. compositions
based mainly on a thermoplastic rubber as previously referred to.

The viscoelastic composition preferably includes a tackifier for promoting bonding of the
spacer to the vitreous sheets.

25 In some embodiments the viscoelastic composition incorporates a hot-melt adhesive.
Such substances can also promote bonding to the vitreous sheets. Ethylene/vinyl acetate
copolymers which have been referred to as useful polymer bases for the viscoelastic
composition also fall in the category of hot melt adhesives.

30 Various other types of ingredients can be incorporated in the viscoelastic ribbon, e.g. a
filler for improving mechanical strength, a vulcanisation inhibitor or retarder, a drying
agent, a substance such as carbon black to function as an ultraviolet radiation screen, and a
plasticiser.

For achieving a very durable bond between the spacer and the vitreous sheets it is
35 recommended to apply a primer coating to the vitreous sheets where the spacer is to be
located. A silane coating is particularly suitable for that purpose.

In some methods according to the invention at least one desiccant-containing strip is laid
adjacent to the viscoelastic ribbon so that the desiccant-containing strip is located internally
of the panel. The incorporation of the desiccant-containing strip improves the performance
of the panel, assuming of course that it is one which is hermetically sealed. Advantageously
40 there is at least one said desiccant-containing strip which comprises a desiccant distributed
in a water-permeable binder. The desiccant increases the resistance of the sealed panel to
deteriorations in optical properties or structure by the effects of moisture. By incorporating
the desiccant into a strip the incorporation of the desiccant into the panel is facilitated and a
very favourable distribution of the desiccant can be ensured. The desiccant binder can be
45 based on one or more synthetic elastomers, preferably one or more butyl rubbers, an
ethylene/vinyl acetate copolymer of polyvinyl chloride, to mention a few examples. The
binder may furthermore incorporate a hot melt adhesive e.g. an ethylene/vinyl acetate
copolymer or some other ingredient serving as a tackifier to assist adhesion of the
desiccant-containing strip to the viscoelastic spacer ribbon if that adhesion is required.

50 Advantageously the desiccant-containing strip or strips and the viscoelastic ribbon are
caused to adhere to each other as or before the ribbon is laid on one of the vitreous sheets
during the panel assembly operation. In some embodiments the desiccant-containing strip is
an extruded strip. The viscoelastic spacer ribbon and the desiccant-containing strip can be
co-extruded and caused to adhere as the ribbon is fed to or laid upon the said vitreous sheet.

55 An alternative or in addition to incorporating a separate desiccant-containing strip in
the panel, a desiccant can be incorporated in the viscoelastic ribbon which is to form the
spacer. Of course desiccant can be incorporated in the panel in some other way. For
example an air-pervious envelope filled with desiccant can be installed in the panel during
assembly.

60 Various further advantages features for ribbons to be used in a method according to the
invention are set out in claims 21 to 29 of this specification. We refer in particular to ribbon
compositions comprising a mixture of polymeric substances in substantially different
molecular weight categories (the higher molecular weight category polymeric material(s)
being curvable) as hereinbefore mentioned and wherein the weight ratio of the relatively low
65 molecular weight category polymeric material(s) to the high molecular weight polymeric

material(s) is between 0.5:1 and 1.6:1; also to ribbon compositions in which the weight ratio of the relatively low molecular weight category polymeric material(s) to the relatively high molecular weight category polymeric material(s) is higher than 2.5:1 and the relatively low molecular weight category polymeric material(s) is or are curable.

5 There are certain combinations of polymers which afford particularly good results. These 5
include: (a) a butyl rubber in combination with an ethylene/vinyl acetate copolymer or a
polyisobutylene which is of substantially higher or lower molecular weight than said butyl
rubber, and in particular a butyl rubber with a molecular weight between 400,000 and
10 600,000 in combination with polyisobutylene having a molecular weight substantially below 10
that range or a butyl rubber with a molecular weight between 5000 and 50,000 in
combination with an ethylene/vinylacetate copolymer having a molecular weight substan-
tially above that range; (b) an ethylene/propylene/diene terpolymer in combination with a
polyisobutylene of substantially lower molecular weight than such terpolymer; (c) a
15 depolymerised butyl rubber and an ethylene/vinyl acetate copolymer of substantially 15
higher molecular weight than such polymer.

The foregoing types of polymer combinations are not exhaustive of what can be used but
with suitable selection of the relative proportions of the different components of the
combination, ribbons which are particularly efficacious for the purposes in view can be
produced. The optimum proportions of such polymer components for any given
20 composition will depend in part on the nature and proportion of the other ingredients of the 20
composition and in particular on the nature and proportion of other polymeric material (if
any) in that composition. Various examples of ribbon compositions, illustrating the above
types of polymer combinations, are given below.

In the following examples, Example 1 is an example of a panel manufacturing method
25 according to the invention, Examples 2 to 9 are examples of viscoelastic ribbons suitable for 25
use in a panel manufacturing method according to the invention in which viscoelastic
ribbons are used for forming an inter-sheet spacer and for sealing the panel in a frame.

The following are the commercial sources of various substances used in those examples
and the general nature of those substances which are identified by Trade Marks: "Butyl
30 LM", "Butyl 268" and "Butyl LM 430": vulcanisable isoprene/isobutylene copolymers 30
marketed by ESSO; "EVA" and "EVA 506B": hot melt adhesives marketed by UNION
CARBIDE; "Methylon" AP 108: phenolic resin tackifier marketed by GENERAL
ELECTRIC; "Escorez" and "Escorez S 280": hydrocarbon resin tackifiers marketed by
ESSO; "Caloxol W5 G": calcium oxide desiccant marketed by STURGE CHEMICALS;
35 "Levilite": silica gel desiccant marketed by RHONE PROGIL; Molecular Sieve desiccant 35
marketed by UNION CARBIDE; "Tonox": vulcanisation inhibitor comprising p,p'-
diaminodiphenylmethane and m. aminoaniline marketed by UNIROYAL; GMF: p-
quinone dioxime vulcanising agent marketed by UNIROYAL; OMYA EXH1: chalk
diluent marketed by OMYA; "Noir P33": carbon black filler marketed by VANDER-
40 BILT; "Noir SOF": carbon black filler marketed by CABOT; PbO₂, PbO₂HC₆, MnO₂: 40
accelerators for GMF vulcanising agent, marketed by RIEDEL DE HAEN; "Shellflex":
plasticisers marketed by SHELL; "Dutral Ter 054/EM": vulcanisable ethylene/propylene/
ethylidene norbornene terpolymer marketed by MONTEDISON; "Vistanex LMMS" and
"VISTANEX 140": non-vulcanisable polyisobutylene marketed by ESSO; "Sunpar 2280":
45 plasticising oil marketed by SUN OIL COMPANY; "Protector G3108": antioxidant wax 45
sold by FULLER; "Anox HB": antioxidant marketed by BOZZETTO; "Indopol H300":
non-vulcanisable polybutene marketed by AMOCO; Glycerol ester rosin adhesive
marketed by TENNECO; "Kalene 800" vulcanisable depolymerised butyl rubber marketed
50 by HARDMAN. 50

Example 1

The glazing unit shown in Figure 1 comprises two sheets of glass 1 and 2 secured in spaced
relationship to a spacer 3 which hermetically encloses the space between the two sheets.

55 For the formation of the spacer an extrudable composition was prepared having the 55
following ingredients:

| | | Parts by weight | |
|----|--|-----------------|----|
| | Butyl LM | 100 | |
| 5 | Butyl 268 | 8 | 5 |
| | EVA ethylene/vinyl acetate copolymer containing 28% by weight vinyl acetate units and constituting a hot melt adhesive | 30 | |
| 10 | "Methylon" AP 108 (phenolic resin tackifier) | 3 | 10 |
| | "Escorez" (hydrocarbon resin tackifier) | 5 | |
| 15 | "Caloxol W 5 G " (Calcium oxide drying agent) | 8 | 15 |
| | "Levillite" (silica gel desiccant) | 20 | |
| | Molecular sieve desiccant (KA1Si0 ₃) | 5 | |
| 20 | "Tonox" (vulcanisation inhibitor) | 2 | 20 |
| | GMF (p-quinone dioxime) vulcanising agent | 3 | |
| 25 | OMYA EXH1 chalk | 10 | 25 |
| | Carbon black | 5 | |
| | PbO ₂ (vulcanisation accelerator) | 9 | |
| 30 | "Shellflex" plasticiser | 4.5 | 30 |

The mutually soluble butyl polymers were mixed together at 130°C and mixing was continued while all of the other ingredients, with the exception of the vulcanisation accelerator, were added. The vulcanisation accelerator was dispersed in the plasticiser and the resulting suspension was then mixed with the mixture of the other ingredients at 60°C. The resulting composition, which had a viscosity at 80°C of between 40,000 and 120,000 poises (estimated as hereinbefore described), was extruded at 60°C to form an extruded ribbon having basically a rectangular cross-section with required corners measuring 10mm × 9mm. This ribbon had a tensile strength of 1 kg/cm² and an elongation at break exceeding 800%. The ribbon was wound onto a core surfaced with silicone paper. After some days, a length of the extruded ribbon 4 was drawn from the coil and laid progressively along the margins of glass sheet 1 as represented in Figure 2, which margins had been coated with amino-silane primer. The second glass sheet 2 which had been similarly marginally primed was then laid onto the applied viscoelastic ribbon. The ribbon supported the second glass sheet without undergoing any perceptible deformation under the supported weight. This assembly took place at room temperature. The assembly was then passed beneath a roller 5 (Figure 3) located to exert downward pressure on the assembly to reduce the thickness of the ribbon (inter-sheet distance) from 10mm to 8mm. The assembly was then placed in an oven for 2 hours at 80°C. This heat-treatment brought about the vulcanisation of the ribbon to form the spacer 3. At the same time the ribbon became very firmly bonded to the glass sheets. Tests on similarly composed and treated ribbon material showed that the vulcanised ribbon had a tensile strength of 16 kg/cm², an elongation at break of 400% and a water permeability of the polymer of 0.02g of water per m² of surface per 24 hours per mm of material thickness per cm of Hg pressure. During manufacture of the glazing unit the vulcanised ribbon was pierced and pressure equalisation between the interior of the unit and the environment was brought about in accordance with known practice in hollow glazing unit manufacture. The pierced hole(s) can very easily be resealed by local heating of the ribbon or by plugging or patching.

In a modification of the foregoing method the extruded viscoelastic composition was formulated as above except that the "Levillite" and the molecular sieve desiccants were omitted and the amounts of carbon black and "OMYA EXH1" were increased by a corresponding aggregate amount. During the assembly of a glazing unit using this modified extruded composition, a quantity of desiccant was enclosed in the unit. The desiccant was dispersed in water-permeable binder, e.g. a binder based on one or more synthetic

elastomers, forming a strip which was disposed just inside the course along which the extruded ribbon was laid.

Example 2

| | | | |
|----|--|-----|----|
| 5 | An extrudable viscoelastic composition was prepared having the following composition in parts by weight: | | 5 |
| 10 | “Dutral Ter 054/EM” terpolymer (an ethylene/propylene/diene terpolymer) | 100 | 10 |
| | Vistanex LMMS (polyisobutylene of molecular weight 8,700 - 10,000) | 100 | |
| 15 | Sunpar 2280 (plasticising oil) | 54 | 15 |
| | Protektor G3108 (anti-oxidant wax) | 3.5 | |
| | Methylon AP108 (phenolic resin tackifier) | 3 | |
| 20 | Escorez S 280 (hydrocarbon resin tackifier) | 5 | 20 |
| | Anox HB (anti-oxidant) | 2 | |
| 25 | GMF (p-quinone dioxime) vulcanising agent | 4 | 25 |
| | OMYA EXH1 chalk | 20 | |
| | “Levilite” (silica gel desiccant) | 20 | |
| 30 | Noir SOF (carbon black filler) | 15 | 30 |
| | Molecular Sieve 4A (dehydrating agent controlling rate of vulcanisation) | 1 | |
| 35 | EVA 506 B (ethylene/vinyl acetate copolymer) | 15 | 35 |
| | Indopol H300 (polybutene) | 20 | |
| 40 | Glycerol ester rosin (adhesive) | 5 | 40 |
| | PbO ₂ HC6 (vulcanisation accelerator) | 6 | |
| | Shellflex 451 (NC (plasticiser) | 2 | |

45 The composition had at 80°C a viscosity corresponding to a torque of 400 g.m. estimated by the Brabender Plastograph Type 50. The composition was extruded at 60°C to form a ribbon of cross-sectional dimensions suitable for use as an inter-sheet spacer in a hollow glass panel. 45

50 A specimen piece of the ribbon was heated at 80°C for 3 hours. This treatment vulcanised the ribbon. The vulcanised ribbon was found to have a tensile strength of 6 kg/cm², an elongation at break in excess of 150% and a water permeability of 0.1g water per m² of surface per 24 hours per mm of material thickness per cm of Hg pressure. 50

Example 3

55 An extrudable viscoelastic composition was prepared as in Example 1 but with the following modifications: The 100 parts by weight of Dutral Ter 054/EM” terpolymer was replaced by 100 parts by weight of Butyl 268 (butyl rubber with a molecular weight of 450,000 to 520,000); the amount of Sunpar 2280 plasticising oil was reduced to 50 parts by weight; the EVA 506 B, Indopol H300 and glycerol ester rosin adhesive were omitted. 55

60 This modified composition had at 80°C a similar viscosity. The composition was extruded at 60°C to form a ribbon for use as an inter-sheet spacer and the extruded ribbon was subjected to a vulcanising treatment as performed in Example 1. The vulcanised ribbon had the following properties: 60

| | | | |
|---|----------------------|--|---|
| | Tensile strength: | 15 kg/cm ² | |
| | Elongation at break: | above 100% | |
| 5 | Water permeability: | about 0.1 g/m ² /24 hours/ mm/cm of Hg | 5 |

Example 4

10 An extrudable viscoelastic composition was prepared having the following composition in parts by weight: 10

| | | | |
|----|---|-----|----|
| | Kalene 800 (depolymerised butyl:) | 100 | |
| 15 | EVA (ethylene/vinyl acetate copolymer containing 28% by weight vinyl acetate units) | 30 | 15 |
| | Vistanex 140 (polyisobutylene of molecular weight between 117,000 and 135,000) | 4 | |
| 20 | Butyl B268 polymer (molecular weight: 450,000-520,000) | 4 | 20 |
| | Protector G3108 (anti-oxidant wax) | 3.5 | |
| 25 | Escorex S 280 (hydrocarbon resin tackifier) | 5 | 25 |
| | GMF (p-quinone dioxime) vulcanising agent | 3 | |
| 30 | OMYA EH1 chalk | 20 | 30 |
| | Noir SOF (carbon black filler) | 20 | |
| | "Levilite" (silica gel desiccant) | 20 | |
| 35 | Molecular Sieve 4A (dehydrating agent controlling vulcanisation rate) | 1 | 35 |
| | Anox HB (anti-oxidant) | 2 | |
| 40 | Methylon AP 108 (phenolic resin tackifier) | 3 | 40 |
| | PbO ₂ HC6 (vulcanisation accelerator) | 6 | |
| 45 | Shellflex 451 NC (plasticiser) | 2 | 45 |

This composition had a viscosity at 80°C of the same order as the composition of Example 1. The composition was extruded and vulcanised by heating at 80°C for 3 hours. The vulcanised ribbon had the following properties:

| | | | |
|----|----------------------|---|----|
| 50 | Tensile strength: | 10 kg/cm ² | 50 |
| | Elongation at break: | 230% | |
| 55 | Water permeability: | about 0.1g/cm ² /24 hours/ mm/cm of Hg. | 55 |

Example 5

An extrudable viscoelastic composition was prepared having the following composition in parts by weight:

| | | | |
|----|---|-----|----|
| 5 | Dutral Ter 054/EM | 100 | 5 |
| | Vistanex LMMS | 100 | |
| | Sunpar 2280 | 54 | |
| 10 | Protektor G3108 | 3.5 | 10 |
| | Escorez S 280 | 5 | |
| 15 | EVA 506 B | 15 | 15 |
| | Glycerol ester rosin | 5 | |
| 20 | “Tonox” aromatic amine vulcanisation retarder | 2 | 20 |
| | GMF | 4 | |
| | OMYA EXH1 | 20 | |
| 25 | Methylon AP 108 | 3 | 25 |
| | Noir SOF | 10 | |
| 30 | Noir P33 (thermal semi-reinforcing filler) | 30 | 30 |
| | Molecular Sieve 4A | 1 | |
| 35 | Indopol H300 | 20 | 35 |
| | MnO ₂ (vulcanisation accelerator) | 6 | |
| | Shellflex 451 NC | 6 | |
| 40 | | | 40 |

The composition was extruded and vulcanised in the same way as the composition in Example 2 and the vulcanised ribbon has similar properties to the vulcanised ribbon in that Example.

45 *Example 6* 45

An extrudable viscoelastic composition was prepared as in Example 5 except that 100 parts by weight of Butyl B268 were used in place of the 100 parts by weight of Dutral Ter 054/EM. The composition had at 80°C a viscosity similar to that of the composition used in Example 3. The composition was extruded at 60°C to form a ribbon and the ribbon was vulcanised by heating at 80°C for 3 hours. The vulcanised ribbon had properties similar to those of the vulcanised ribbon in Example 3. 50 50

60 *Example 7* 60

An extrudable viscoelastic composition was prepared as in Example 5 with however the following modifications: The composition contained 10 instead of 20 parts by weight of OMYA EXH1, 20 instead of 10 parts by weight of Noir SOF, and nil Noir P33; the composition further included 20 parts by weight of Levilite and 2 parts by weight of Anox HB, and contained 6 parts by weight of PbO₂ HC6 instead of 6 parts by weight of MnO₂, and 2 parts instead of 6 parts by weight of Shellflex 451 NC. 55 55

The viscosity of the composition was of the same order as that of the composition in Examples 2 and 5. The composition was extruded to form a ribbon and the ribbon was vulcanised by heating at 80°C for 3 hours. The vulcanised ribbon had properties similar to those of the vulcanised ribbon in Examples 2 and 5. 60 60

Example 8

A viscoelastic composition was prepared having the following composition in parts by weight:

| | | | |
|----|----------------------|-----|----|
| 5 | Butyl B268 | 100 | 5 |
| | Vistanex LMMS | 100 | |
| | Sunpar 2280 | 50 | |
| 10 | Protektor G3108 | 3.5 | 10 |
| | Escorez S 280 | 5 | |
| 15 | Tonox | 2 | 15 |
| | GMF | 4 | |
| | OMYA EXH1 | 20 | |
| 20 | Noir SOF | 15 | 20 |
| | Molecular Sieve 4A | 1 | |
| 25 | Levilite | 20 | 25 |
| | Methylon AP108 | 3 | |
| | Anox HB | 2 | |
| 30 | PbO ₂ HC6 | 6 | 30 |
| | Shellflex 451 NC | 2 | |

35 The composition had a viscosity of the same order as that of the composition in Example 3. 35
The composition was extruded at 60°C to form a ribbon. The ribbon was vulcanised by heating at 80°C for 2 hours. The vulcanised ribbon had properties similar to those of the vulcanised ribbon in Example 3.

Example 9

A viscoelastic composition was prepared having the following composition in parts by weight:

| | | | |
|----|---|-----|----|
| 5 | Butyl LM 430 (butyl polymer with a molecular weight of 38,000 - 40,000) | 100 | 5 |
| | EVA 506 B | 30 | |
| 10 | Butyl B 268 | 8 | 10 |
| | Protektor G 3108 | 3.5 | |
| | Escorez S 280 | 5 | |
| 15 | Tonox | 2 | 15 |
| | GMF | 3 | |
| 20 | OMYA EXH1 | 20 | 20 |
| | Noir SOF | 20 | |
| | Molecular Sieve 4A | 1 | |
| 25 | Methylon AP 108 | 3 | 25 |
| | MnO ₂ | 7.5 | |
| 30 | Shellflex 451 NC | 7.5 | 30 |

This composition had a viscosity similar to that of the composition in Example 1. The composition was extruded at 60°C to form a ribbon. The ribbon was vulcanised by heating at 80°C for a minimum of 2 hours. The vulcanised ribbon had the following properties:

| | | | |
|----|---------------------|--|----|
| 35 | Tensile strength | 10 kg/cm ² | 35 |
| | Elongation at break | well above 100% | |
| 40 | Water permeability | 0.08g/cm ² /24 hours/mm/cm of Hg. | 40 |

Example 10

A hollow glazing unit as shown in Figure 4 was manufactured as follows: A frame component 8 was primed by application of a primer coat to the face to be contacted by a sealing strip 9. The sealing 9, which was extruded from a composition as used in Example 1, was laid on the primed face of the frame component 8 and a marginally primed glass sheet 10 was placed in position to sandwich the strip 9 between that sheet and the frame component and subject the strip to sufficient pressure to deform it and ensure film contact of the glass sheet and the frame component 8 with the said strip. This sub-assembly was then heated for 24 hours at 80°C to vulcanise the sealing strip and bring about its firm bonding to the glass sheet and the frame component. A second sub-assembly, comprising glass sheet 11, sealing strip 12 and frame component 13 was made in an identical manner. The two sub-assemblies were then connected together by bolts such as 14, screwed into threaded sockets in the frame components 8 and 13, after positioning a spacer ribbon 15 between the internal marginal faces of the two sheets of glass, which faces had been primed with an amino-silane primer. Ribbon 15 had been extruded from the same composition as that used for sealing strips 9 and 12. This ribbon 15 has a cross-section such that it became deformed and forced into firm contact with the glass sheets as the frame components became firmly bolted together. The complete assembly was then heated for 2 hours at 80°C to bring about vulcanisation of strip 15 and its firm bonding to the glass.

Viscoelastic ribbons having a composition according to any of Examples 2 to 9 can be used in place of the viscoelastic ribbons 9, 12 and 15 in the above Example 10.

In a modification of the method according to Example 10, the sealing strips 9 and 12 were not vulcanised prior to connecting the sub-assemblies together. After such connection, a single vulcanisation step was carried out to vulcanise the strips 9, 12 and the ribbon 15

simultaneously.

In a further modification of the said method, the spacer ribbon 15 was omitted and reliance was placed on the strips 9 and 12 and their firm bondage to the glass sheets and the frame components for air-tightly and moisture-tightly sealing the hollow unit.

5 In certain glazing units according to the invention, glass sheets were secured in spaced relationship by means of a cured spacer ribbon which was inset from the edges of the glass sheets and the groove between the projecting margins of the glass sheets was filled with a polyvinylidene chloride mastic to provide an additional moisture barrier and/or for any other required purpose.

10 WHAT WE CLAIM IS:

1. A method of manufacturing a hollow panel by uniting vitreous sheets by means of a spacer of synthetic polymeric material located between and adherent to margins of such sheets, characterised in that a spacer with a tensile strength of at least 4 kg/cm², an elongation at break in excess of 50% and a water permeability of the polymeric material less than 0.2 g of water per m² of surface per 2 hours per mm of material thickness per cm of Hg pressure is formed in situ from a hardenable viscoelastic ribbon which has cross-sectional dimension and a viscosity sufficient to maintain the two vitreous sheets at at least the required final inter-sheet spacing under the weight of the superimposed sheet when the sheets are disposed horizontally with the ribbon between them, the panel being formed by laying said ribbon upon the margin of one of the sheets, laying the other sheet in position, supported by the ribbon, and then subjecting said ribbon to hardening conditions to convert it into said spacer while the vitreous sheets are at said final required spacing.

2. A method according to claim 1, characterised in that said viscoelastic ribbon is extruded onto the margin of said one sheet.

3. A method according to claim 1 or 2, characterised in that the thickness of the ribbon (measured in a direction normal to the vitreous sheets between which it is located preparatory to the hardening operation) is in excess of the said required final inter-sheet spacing and pressure is exerted on the assembly to bring the inter-sheet spacing to that required value before the ribbon is converted into said spacer.

4. A method according to claim 3, characterised in that said pressure is exerted by bringing about relative horizontal displacement between a support on which the assembly is located and at least one roller which is spaced above said support by a distance equal to the required final overall thickness of the panel, to cause said roller(s) to bear against the upper vitreous sheet.

5. A method according to any preceding claim, characterised in that the composition forming said viscoelastic ribbon has at 80°C a viscosity of 40,000 to 120,000 poises estimated by means of a Brabender plastograph test as herein defined.

6. A method according to any preceding claim, characterised in that the viscoelastic ribbon has a tensile strength of from 0.5 to 3 kg/cm².

7. A method according to any preceding claim, characterised in that the viscoelastic ribbon has an elongation at break in excess of 700%.

8. A method according to any preceding claim, characterised in that the composition of said viscoelastic ribbon and said hardening conditions are such that the spacer has a tensile strength of from 4 to 50 kg/cm².

9. A method according to claim 8, characterised in that the composition of said viscoelastic ribbon and said hardening conditions are such that the spacer has a tensile strength of at least 10 kg/cm².

10. A method according to any preceding claim, characterised in that the composition of said viscoelastic ribbon and said hardening conditions are such that the spacer has an elongation at break exceeding 100%.

11. A method according to claim 10, characterised in that the composition of said viscoelastic ribbon and said hardening conditions are such that said spacer has an elongation at break of from 150 to 450%.

12. A method according to any preceding claim, characterised in that said viscoelastic ribbon is capable of being and is in fact cured at less than 100°C to form said spacer in situ.

13. A method according to claim 12, characterised in that said viscoelastic ribbon incorporates a mixture of polymeric substances in substantially different molecular weight categories.

14. A method according to any preceding claim, characterised in that said viscoelastic ribbon incorporates a tackifier.

15. A method according to any preceding claim, characterised in that said viscoelastic ribbon incorporates a hot melt adhesive.

16. A method according to any preceding claim, characterised in that at least one desiccant-containing strip is laid adjacent to the said ribbon so that the desiccant-containing strip is located internally of the panel.

17. A method according to claim 16, characterised in that there is at least one said desiccant-containing strip comprising a desiccant distributed in a water-permeable binder.

18. A method according to claim 16 or 17, characterised in that the or each desiccant-containing strip is caused to adhere to said ribbon.

19. A method according to claim 18, characterised in that the desiccant-containing strip or strips and the ribbon are caused to adhere to each other as or before said ribbon is laid on said one vitreous sheet.

20. A method according to any of claims 16 to 19, characterised in that said desiccant-containing strip is an extruded strip.

21. A method according to any preceding claim, wherein the ribbon composition comprises a mixture of at least one curable polymeric material with at least one polymeric material, in a substantially lower molecular weight category than said curable polymeric material(s) and the weight ratio of the relatively low molecular weight category polymeric material(s) to the relatively high molecular weight category polymeric material(s) is between 0.5:1 and 1.6:1.

22. A method according to any of claims 1 to 20, wherein the ribbon composition comprises a mixture of at least one curable polymeric material with at least one polymeric material in a substantially higher molecular weight category than said curable polymeric material(s) and the weight ratio of the relatively low molecular weight category polymeric material(s) to the relatively high molecular weight category polymeric material(s) is higher than 2.5:1.

23. A method according to claim 21 or 22, wherein the ribbon composition is based on a mixture of polymers comprising at least one butyl rubber.

24. A method according to claim 22, wherein the ribbon composition is based on a mixture of polymers comprising at least one butyl rubber of a molecular weight between 5000 and 50,000 and at least one butyl rubber of molecular weight between 400,000 and 600,000.

25. A method according to claim 23, wherein the ribbon composition is based on a mixture of polymers comprising butyl rubber and a polymer which is of substantially higher or lower molecular weight than said butyl rubber and is selected from ethylene/vinyl acetate copolymers and polyisobutylene.

26. A method according to claim 25, wherein the ribbon composition is based on a mixture of polymers comprising a butyl rubber with a molecular weight between 400,000 and 600,000 and a polyisobutylene having a molecular weight substantially below that range.

27. A method according to claim 22, wherein the ribbon composition is based on a mixture of polymers comprising a butyl rubber with a molecular weight between 5000 and 50,000 and an ethylene/vinylacetate copolymer having a molecular weight substantially above that range.

28. A method according to claim 21, wherein the ribbon composition is based on a mixture of polymers comprising an ethylene/propylene/diene terpolymer and a polyisobutylene of substantially lower molecular weight than such terpolymer.

29. A method according to claim 22, wherein the ribbon composition is based on a mixture of polymers comprising a depolymerised butyl rubber and an ethylene/vinylacetate copolymer of substantially higher molecular weight than such polymer.

30. A method of manufacturing a hollow panel, substantially according to Example 1 or Example 10 herein.

31. A method according to claim 1 of manufacturing a hollow panel, wherein a viscoelastic ribbon substantially according to any of Examples 2 to 9 herein.

32. A hollow panel manufactured by means of a method according to any preceding claim.

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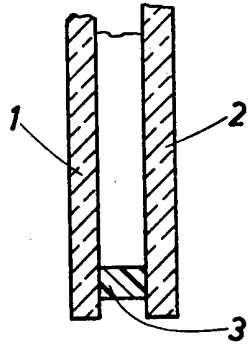


Fig. 1.

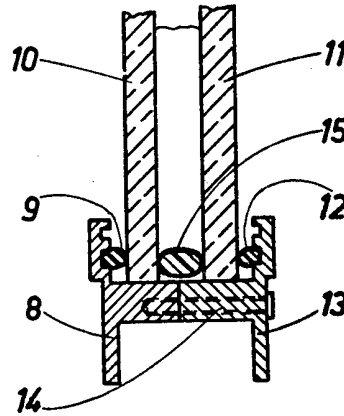


Fig. 4.

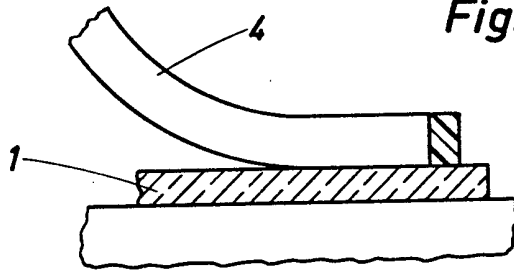


Fig. 2.

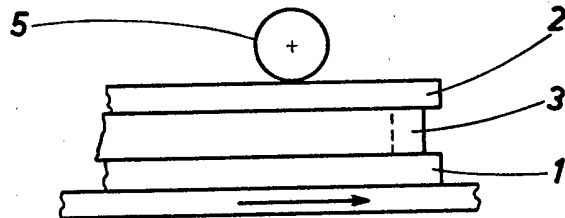


Fig. 3.