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Flexible preformed adhesive strip, window structure and laminate.

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Description

BACKGROUND OF THE INVENTION

i) Field of the Invention

This invention relates to a flexible preformed adhesive strip comprising an adhesive layer, said layer comprising an essentially solvent-free adhesive composition, said adhesive composition can be cured on command or at a desired point in time.

In particular the invention is concerned with an adhesive strip comprising a composition curable by curing radiation, but in which the surface cure is inhibited by oxygen. This invention further relates to a window structure comprising an adhesive layer, said layer comprising said adhesive composition. Furthermore, this invention provides a laminate comprising an adhesive layer, said layer comprising said adhesive composition.

ii) Description of the Prior Art

Adhesive compositions are employed in a variety of environments in which a bond or seal is to be formed between two closely spaced surfaces, and in the manufacture of laminates of different materials. They may be applied in a flowable form, for example, as a liquid, and allowed to cure or set to a solid mass in situ; or they may be applied in a tape form in which the adhesive composition forms a coating or layer on a supporting substrate or film.

Such compositions are usually multi-component formulations in which two or more components are admixed at the time of use whereafter chemical reaction between the components to form a cured composition commences. If the cure proceeds rapidly the formulation must be employed without delay. If cure retardants are employed to delay or retard the cure, prolonged periods are required to complete the cure, and in some cases this means that the product must be stored in a controlled atmosphere over a period of days to allow the cure to complete.

Various mastic products, for example, sealants and preformed tapes and strips are known for mounting window glass. These mastic products are employed to bond sheets of window glass together adjacent their peripheral edges, in spaced apart relationship with an air space therebetween; they are also employed as bonding mediums and sealants between the window glass and the supporting frame structure which is typically of metal.

The problems associated with retarded cure of adhesives are experienced in the window industry with these mastic products wherein stacks comprising pairs of bonded together window glass must be stored for several days to allow the cure to complete.

These mastic products contain a solvent and are flowable, uncured polymer materials. The flowable nature presents handling problems and may also result in undesirable migration of the polymer material across the window glass surface, which is aesthetically unacceptable.

EP-A-0 134 677 teaches a radiation decomposable compound which decomposes to a strong acid, and this strong acid drives a curing reaction without the need for further radiation, once oxygen is removed. The chemistry of the present invention is distinguishable, because it requires that the composition be "curable only while being exposed to said curing radiation".

With the EP-reference, once the composition is exposed to UV light, the composition must be exposed to oxygen until it is applied to its intended substrate, otherwise the composition will cure prematurely. With the chemistry of the present invention, the composition can be exposed to UV but will not cure until there is oxygen inhibition and exposure to UV light.

In addition to their adhesive character, these mastic products are required to display other characteristics having regard to the environment in which they are to be used. Thus mastic products employed as sealants in window structures should be weather resistant and impermeable to moisture and water.

SUMMARY OF THE INVENTION

The invention contemplates a strip, a window structure and a laminate comprising a composition which provides a so-called "command-cure" of a non-bonding polymer composition, whereby the composition is rendered adhesively bonding.

The expression "command-cure" contemplates that an otherwise non-bonding-polymer composition is rendered adhesively bonding at a selected point in time. The point in time is chosen by the user of the
composition.

The expression "non-bonding polymer composition" contemplates a composition in a state in which it does not form a firm adhesive bond sufficient to permanently secure two layers together; the composition may, however, be sufficiently adhesive or tacky to form a weak bonding between layers, sufficient as a temporary holding means during careful assembly and handling. The expression "adhesively bonding" contemplates a composition in a state in which it forms a firm, substantially permanent bond.

Thus in one aspect the invention provides a method of bonding self-supporting layers in opposed facing relationship which comprises introducing a non-bonding polymer composition adapted to be rendered adhesively bonding between opposed surfaces of the layers to form an assembly and subsequently rendering the composition adhesively bonding at a selected time interval after formation of the assembly to firmly bond together the opposed surfaces of the layers.

In one embodiment there is provided a flexible, preformed adhesive strip comprising:
- a flexible substrate and an adhesive layer supported on said substrate,
- said adhesive layer having a shaped body portion and a first outer surface portion remote from said substrate,
- said adhesive layer being transparent to curing radiation and having a thickness of up to twice its transparent depth and comprising an essentially solvent-free adhesive polymer composition, being substantially cured throughout said body portion and uncured at said first outer surface portion, such that said first outer surface portion remains tacky,
- said adhesive layer comprising an acrylate polymer with a plurality of pendant side chains containing terminal vinyl groups sufficient to provide cross-linking and a cross-linking agent for said polymer and being curable by UV-radiation in the range of 250 to 450 nm only while being exposed to said curing radiation to produce a cured composition and having a transparent depth up to 2.54 cm (1 inch), the curing of said adhesive polymer composition by said radiation being inhibited by oxygen.

In another embodiment of the invention there is provided a window structure comprising first and second surfaces, at least said first surface comprising a transparent pane, said surfaces being in opposed facing relationship and an adhesive layer bonding said surface therebetween, said adhesive layer comprising a shaped substantially precured body being transparent to curing radiation and having a thickness of up to twice its transparent depth and comprising an essentially solvent-free adhesive polymer composition,
- said adhesive polymer composition comprising an acrylate polymer having a plurality of pendant side chains containing terminal vinyl groups present in a predominant amount and a cross-linking agent for said polymer and being curable by UV-radiation in the range of 250 to 450 nm only while being exposed to said curing radiation to produce a cured essentially water resistant composition and having a transparent depth up to 2.54 cm (1 inch), the curing of said adhesive polymer composition by said radiation being inhibited by oxygen.

In another embodiment there is provided a laminate comprising:
- first and second self-supporting layers in opposed facing relationship and an adhesive layer therebetween;
- said adhesive layer having a pre-shaped body portion and opposed first and second outer surface portions, said outer surface portions being in contacting relationship with said first and second layers respectively,
- said adhesive layer being transparent to curing radiation and having a thickness of up to twice its transparent depth and comprising an essentially solvent-free adhesive polymer composition,
- said adhesive polymer composition comprising an acrylate polymer having a plurality of pendant side chains containing terminal vinyl groups present in a predominant amount and a cross-linking agent for said polymer and being curable by UV-radiation in the range of 250 to 450 nm only while being exposed to said curing radiation to produce a cured essentially water resistant composition and having a transparent depth up to 2.54 cm (1 inch), the curing of said adhesive polymer composition by said radiation being inhibited by oxygen.

The adhesive layer is substantially cured throughout the body portion, and at least partially uncured at the outer surface portions, such that the outer surface portions are sufficiently tacky to provide adhesion between the self-supporting layers and the adhesive layer.

In yet another embodiment there is provided a method of producing an adhesive composition transparent to and curable by curing radiation, the curing being inhibited by oxygen, comprising reacting a long chain polymer material having a plurality of non-terminal side functional groups with a side chain-forming compound having a first end functional group which is reactive with the side functional group, and a second end vinyl group remote from the first end functional group, to form a long chain polymer material having a plurality of short pendant side chains, with terminal vinyl groups, and admixing the long chain
polymer material with a cross-linking agent effective in the presence of curing radiation and absence of oxygen to form cross-linking bridges containing the vinyl groups.

The modified polymer material bearing side chain terminal vinyl groups is flowable, by which is meant that the material is liquid or mobile or can be rendered liquid or mobile at moderate elevated temperatures such that the mixture of modified polymer material, cross-linking agent and other optional additives can be extruded, cast, coated or otherwise applied to a substrate surface.

DESCRIPTION OF PREFERRED EMBODIMENTS

i) COMMAND-CURE

By means of the invention an assembly of two windows, for example, glass or plastic windows, can be formed in which the opposed faces of the windows are held together with the non-bonding polymer composition therebetween, adjacent peripheral edges of the windows, the windows being separated to provide an insulating space therebetween.

The assembly may rely on the tacky nature of at least the surface of the composition to temporarily hold the windows together in opposed facing relationship, and thereafter, at a selected time, the composition may be rendered adhesively bonding to firmly bond the windows together in their opposed facing relationship. The adhesive bonding character may be triggered in several ways, for example, heat, U.V. radiation or microwave radiation.

In accordance with the invention a technique has been developed to provide the "command-cure" feature:

Photo-cure Adhesives

These adhesives are cured in the presence of ultra-violet radiation and the absence of oxygen. Thus a shaped flexible strip may be formed which is cured throughout its body but tacky and uncurd at a surface exposed to oxygen. The tacky surface is applied to a glass surface thereby excluding oxygen. Exposure of the uncurd tacky surface to ultra-violet radiation, at a selected time, results in rapid cure at the surface of the shaped strip to form a firm adhesive bond between the glass surface and the strip. The ultra-violet radiation for the "command-cure" is suitably directed through the glass or through the material itself.

The photo-curable adhesives or sealants are acrylates which polymerize by a free radical mechanism initiated by ultra-violet light. The compounding ingredients employed should suitably be transparent to ultra-violet light in the U.V. range of the spectrum, especially the 300 to 400 nanometer range with particular attention to 365 nanometers which is the frequency of most industrial U.V. ovens.

Adhesives or sealants made with photosensitive monomers can be used in two manners:

i) The entire adhesive or sealant may be comprised of a compounded acrylate.

ii) The acrylate may be coated on a carrier, for example, a pre-cured butyl, neoprene and EPDM rubber which serves as the main body of the sealant system and derives its adhesion from the photosensitive material which is coated onto the contacting surfaces prior to assembly of the insulating glass unit. This can be done either at the time of manufacturing of the sealant system or by the user of the system at the time of application.

Employing system ii) a composite comprising the acrylate coated on a carrier is applied to an insulating glass assembly and cured by exposing the assembly to an ultra-violet light source. This cure is effected in a matter of seconds or minutes depending on the concentration of the light source.

ii) RADIATION-CURABLE ADHESIVE COMPOSITION

Radiation-cure adhesive, especially photo-cure adhesives, represent an especially preferred form of command-cure adhesives.

The adhesive composition is, in particular, a polymer composition comprising an adhesive mixture of a long chain polymer material modified by the introduction of short pendant side chains, which side chains have terminal vinyl groups, and a di- or poly-functional cross-linking agent effective to react with the vinyl groups under appropriate conditions whereby bridges are formed between vinyl groups in different polymer chains to cure the modified polymer material.

In particular, the cross-linking occurs in the presence of curing radiation, and the cross-linking or curing is inhibited by oxygen.
The modified polymer and the cross-linking agent are selected such that an uncured mixture forming the adhesive composition is transparent to the curing radiation to a depth of up to 25.4 (1.0), more generally up to 19.4 mm (0.75 inches). This means that the composition is transparent to the radiation for a depth up to 25.4 mm (1.0 inches) measured from the surface of the composition on which the radiation is incident; this depth is referred to herein as the transparent depth.

More especially the composition will have a transparent depth of not more than 12.7 mm (0.5 inches) and typically not more than 6.4 mm (0.25 inches).

The thickness of the composition which can be cured is proportional to the transparent depth. In particular, the maximum thickness of composition which can be cured is twice the transparent depth of the composition, for the case in which a layer or coating of composition is exposed to the curing radiation from opposite sides of the layer or coating.

Thus the composition can be maintained in the uncured state by excluding the curing radiation, for example, by maintaining the composition in an enclosure opaque to the curing radiation.

The curing of the composition is inhibited by oxygen and so the presence of oxygen dissolved in or otherwise occluded or entrained within the composition is to be avoided. In this regard the composition is suitably substantially free of gaseous oxygen. In so far as the outer surface portion of the composition is open to the atmosphere and thus exposed to oxygen gas, the outer surface portion of the composition will remain tacky even though the body portion is cured under the action of curing radiation penetrating the composition. The tacky surface portion can be adhered to a surface of a substrate so that access of oxygen to the surface portion is excluded. If curing radiation is able to penetrate to the tacky surface, either through the substrate, if it is transparent to the curing radiation, or through the body portion of the cured composition in so far as it is transparent to the radiation, the tacky outer surface portion will be cured. If the substrate is opaque or if, in any event, the tacky portion is not exposed to the curing radiation, it will remain tacky.

The composition suitably has a viscosity of at least 50,000 mPas (cps) and preferably 100,000 mPas (cps) at 25 °C, and is pumpable. The composition is non-sagging in the pumpable state when applied in a thickness of at least 1.58 mm (0.0625 inches). By non-sagging is meant that the composition can be applied in the pumpable state between a window pane and supporting frame separated by a spacing of at least 15.8 mm (0.625 inches), and the composition will fill the space and not flow out.

The composition may contain conventional additives to impart known, desired characteristics, for example, adhesion promoters, plasticizers, photo-initiators, stabilizers, pigments and fillers.

a) Unmodified Polymer

In particular, the unmodified polymer is a long chain polymer material having a M.W. of 2,000 to 100,000, preferably 10,000 to 60,000, and is an acrylate polymer having a plurality of side functional groups selected from carboxyl, hydroxyl, mercapto, acrylonitrile or acrylamide.

Particularly suitable unmodified polymer materials are copolymers, terpolymers and tetrapolymers based on acrylic monomers. Suitable monomers include ethylacrylate, butylacrylate, 2-ethylhexylacrylate, \( \beta \)-carboxyethylacrylate, hydroxypropylacrylate, acrylic acid and acrylonitrile.

b) Modified Polymer

In accordance with the invention the unmodified polymer is modified at the side functional groups to introduce the short pendant side chains bearing the terminal vinyl groups.

The introduction of the short pendant side chains is achieved by a reagent having, on a molecular level, a functional radical at one end of the molecule which will react with a side functional group of the unmodified polymer, and a vinyl group at the other end of the molecule.

The vinyl group in the reagent is preferably an acrylate group. The functional radical reactive with the side functional groups may, in particular, be an epoxy, hydroxy, isocyanate or aziridinyl radical, or a carboxylate of a polyvalent metal.

Suitable reagents include glycidyl methacrylate: zinc diacrylate or dimethacrylate; zinc(hydroxy)acrylate; calcium diacrylate or dimethacrylate; chromium (III) diacrylate or dimethacrylate; zirconium diacrylate or dimethacrylate; tributyl tin acrylate and 2-((1-aziridinyl) ethyl methacrylate, and a reaction product of a disiocyanate and a hydroxyalkylacrylate, for example, methylene-bis-cyclohexyl isocyanate hydroxyalkyl acrylates, for example, hydroxypropyl acrylates.

Thus the modifying reagent may be a metal di-or triacrylate or a metal hydroxy acrylate of formula (I):
in which Me is a metal, A represents an acrylate radical, x is an integer of at least 2, n and m are both integers of at least 1 and $n + m = x$.

The modifying reagent may be an epoxy compound of formula (II):

$$\begin{align*}
\text{CH}_2 \quad \text{CH} \quad (\text{CH}_2)_p \quad \text{A} \\
\end{align*}$$

(II)

in which A is as defined above and $p$ is an integer of at least 1.

The modifying reagent may also be an aziridinyll compound of formula (III):

$$\begin{align*}
\text{N} \quad (\text{CH}_2)^p \quad \text{A} \\
\end{align*}$$

(III)

in which A and $p$ are as defined above.

The modifying reagent may also be an acid of formula (IV):$\text{A} \quad -(\text{CH}_2)_p \quad \text{COOH} \quad \text{(V)}$

wherein A and $p$ are as defined above.

The modifying reagent may also be an isocyanate of formula (V) or (VI):

$$\begin{align*}
\text{OCN} \quad \text{R}^1 \quad \text{A} \\
\text{OCN} \quad \text{R}^1 \quad \text{NHC} \quad \text{O} \quad \text{R}^2 \quad \text{A} \\
\end{align*}$$

(V)

(VI)

wherein $R^1$ and $R^2$ are the same or different and are aliphatic, cycloaliphatic or aromatic structures containing one or more rings; for example, alkylene, cycloalkylene or arylene having a carbon atoms range of 2 to 18.

In particular the acrylate radical A is of formula (VII):

$$\begin{align*}
\text{CH}_2 \quad \text{C} \quad \text{O} \\
\text{R} \quad \text{O} \\
\end{align*}$$

(VII)

in which R is a hydrogen atom or alkyl of 1 to 4 carbon atoms, preferably methyl.

c) Cross-Linking Agent

The cross-linking is effected with a polyfunctional cross-linking agent in which the functional groups react with vinyl groups. A di-functional cross-linking agent will react with pairs of vinyl groups, more especially pairs in which the vinyl groups are in different or separate polymer chains of the polymer material. A trifunctional cross-linking agent can react with up to three such vinyl groups.

By appropriate selection and amount of the cross-linking agent, flexible cross-linking bridges can be formed to cure the modified polymer material to form a resilient or flexible cured adhesive polymer.

The cross-linking agent and terminal vinyl groups are selected such that the curing requires curing radiation, and the complete curing is inhibited by oxygen.

The cross-linking agents are, in particular, selected to match the modified polymer material having regard to the desired characteristics of the adhesive. Particularly suitable cross-linking agents for use with
the acrylate based polymers are di- and tri-acrylates. In this way flexible bridges are formed between the polymer chains which produce resilience and flexibility which is a desirable characteristic for many applications including the mounting of window glass.

Furthermore the di-, tri-, or polyfunctional cross-linking reagent preferably of acrylate functionality, may react with a reactive diluent, for example, a monoacrylate such as caprolactone acrylate or plasticizer and the acrylate functionality of the modified polymer material under radiation conditions to give a cross-linked network of the desirable physical properties. Typical examples of difunctional acrylates are: ethylene glycol diacrylate; diethylene glycol diacrylate; tetramethylene glycol diacrylate; polyethylene glycol diacrylate; 1,3-butylene glycol diacrylate; 1,4-butanediol diacrylate; dimethylene glycol diacrylate; 1,6-hexanediol diacrylate; 2,2-dimethylpropane-1,3-diacylate; tripropylene glycol diacrylate; ethoxylated bis-phenol-A-diacrylate; zinc diacrylate; and their dimethacrylate homologues.

Typical trifunctional acrylates are: trimethylolpropane triacrylate; ethoxylated trimethylolpropane triacrylate; and pentaerythritol triacrylate.

Typical polyfunctional acrylates are: pentaerythritol tetraacrylate; dipentaerythritol monohydroxy pentaacrylate.

Glycidyl methacrylate, glycidyl acrylate and 2-(1-aziridinyl) methacrylate are suitable as polyfunctional acrylates in the presence of chemical species which polymerize the three-membered rings.

The cross-linking agent may also be selected from higher molecular weight acrylates, for example, the so-called urethane acrylic oligomers prepared from di- or tri-functional alcohols (diols and triols) after reaction with excess disiocyanate to give a tri-functional isocyanate and conversion of the isocyanate groups with hydroxyethylacrylate or hydroxypropylacrylate to provide the desired acrylate functionality.

Isocyanate functionality can be introduced with aromatic or aliphatic disiocyanates. Residual isocyanate functionality on these polymers can lead to desirable cross-linking with polyhydroxy components in the formulation. This can be advantageous in applications where the depth of light-initiated cure in the preferred case of cure by UV radiation, is not sufficient or when adhesion to a substrate is required which contains surface functionalities reactive with isocyanates. Such reactive polymers are difunctional, but essentially monofunctional with respect to their isocyanate or acrylate groups; that is, each polymer contains on average one acrylate and one isocyanate group. Similarly, a fraction of the number of the acrylate functionality of the tri- or tetraacrylates can be isocyanate functionality. To increase the efficiency of these isocyanates, conventional catalysts such as tertiary amines can be included in the formulation, or as part of the initiator.

Such isocyanates can also be effective when the polymers contain hydroxy functionality, either as the result of the polymer modification or by using initiators for the polymerization which introduce hydroxy functionality.

The acrylate polymers can be based on polyesters or polyethers with terminal hydroxy functionality or similar polymers with more than two hydroxy groups.

The pendant vinyl groups of the modified polymer themselves permit radiation cross-linking, so that the addition of a di- or polyfunctional cross-linking agent may not be required, depending on the properties, for example, flexibility, desired. For example, when acrylates are used as polymer modifying agents, radiation cross-linking may occur even if the polyfunctional cross-linking agent is not present.

d) Curing Radiation

The curing radiation is suitably UV radiation having wavelengths of between 250 and 800 nm, preferably between 250 and 450 nm. However, electron beam radiation, microwave and heat radiation may also be employed as curing radiation although these are less preferred.

e) Additives

The compositions may contain one or more conventional additives depending on the physical characteristics required including adhesion promoters, plasticizers, photoinitiators, stabilizers, pigments and fillers.

Adhesion promoters are materials which increase the adhesion of the cured product to various surfaces such as glass and metals. Adhesion promoters can be added to the composition or can be co-polymerized into the polymer material.

Typical examples are: acrylic acid, β-carboxyethyl acrylate, silanes and titanates.

The adhesion promoters may also be applied to the surface on which the composition to be applied. It may also be appropriate to apply an adhesion promoting primer, for example, acrylate, amino and
mercapto-functional silanes, for example, mercaptopropyl trimethoxysilane and aminopropyl trimethoxy-
silane and a mixture of aminopropyl trimethoxysilane and a copolymer of butylacrylate-acrylic acid (60:40).

Plasticizers are reactive diluents which increase the flexibility of the cured product particularly at low
5 temperatures. The materials selected are those which can be chemically bound into the network so that the
product contains a minimum level of volatile components. Typical examples of such reactive diluents are:
isodecyl acrylate, isobornyl acrylate, dicyclopentenyloxyethyl acrylate, cyclohexyl acrylate, tetrahydrofur-
furyl acrylate, lauryl acrylate, 2-ethoxyethoxyethyl acrylate, phenoxethyl acrylate, 2-(1-aziridinyl)-ethyl-
methacrylate, N-vinyl-2-pyrrolidone, N-isobutoxymethyl acrylamide.

Photo-initiators are used to increase the rate of cure in the case of cure by UV radiation. The choice of
10 photo-initiator depends on several factors, such as the light source, the presence of fillers in the formulation,
and the desirable colour of the product. Typical examples are: benzophenone, 2,2-diethoxyacetophenone,
diethoxyphenylacetophenone, IRGACURE® 184, (trade mark of Ciba-Geigy for 1-hydroxy)cyclohexyl phenyl
ketone), IRGACURE® 907 (trade mark of Ciba-Geigy for 2-methyl-1-[4-(methylthio)phenyl]-2-mor-
pholino-propanone-1), SANDORAY® 1000 (trade mark of Sandoz), DAROCURE® 1173 (trade mark of E. M.
Chemicals), UV Absorber 0505 (Van Dyke & Co.), CYRACURE® UVI-6990 (trade mark of Union Carbide).

Combinations of initiators and sensitisers can lead to synergistic effects. Particularly effective are
15 combinations of aryl ketones and a tertiary alkanolamine such as N-methylidethanolamine. Alternatively, the
photoinitiator may contain both functional groups. Other co-initiators are methyloxanthone and the ethyl
ester of p-dimethylaminobenzoic acid.

If the photo-initiator is insoluble in the acrylate, it may be advisable to dissolve it in a component of
20 the formulation rather than in the total mixture to be photo-cured.

Stabilizers improve the weathering characteristics of the cured product; it may be advantageous to add
photo-antidegradants. A suitable combination, for instance, consists of, by weight, 2% of Irgacure® 184 and
0.5% of Tinuvin® 292, both trade marks of Ciba-Geigy.

Pigments and fillers are selected for different purposes. Light-transparent fillers such as silica are
25 preferred if the penetration of UV light into deeper sections of a photo-curable material is required.

However, the filler may be chosen to be such that it participates in the cross-linking. In the case of
photo-cross-linking this can be achieved by using metal salts of photo-cross-linkable acids such as the zinc
salts of acrylic acid, methacrylic acid and β-carboxyethyl acrylic acid.

f) Methods

In manufacturing the unmodified polymer material the monomers are polymerized in the absence of a
30 solvent or in the presence of a solvent which can be readily removed after polymerization, for example,
toluene or xylene. If no solvent is employed, the initiator for the polymerization is dissolved in the monomer
mixture, which usually requires cooling the mixture to maintain a temperature at or below 25°C. during the
polymerization; or the initiator is metered into the reaction mixture during the polymerization, the level of
inhibitor is also controlled and maintained.

In the absence of solvent, viscosity of the polymerization mixture increases as the polymerization
35 proceeds resulting in the need for high torque mixing.

Suitable polymer materials which are designed to become cross-linkable after modification, especially
photo-cross-linkable are based on acrylic monomers such as methylacrylate, ethylacrylate, butylacrylate
and hydroxypropylacrylate and their homologues as well as the corresponding methacrylates.

As indicated the polymerization may be carried out with or without solvent. If a solvent is selected, its
40 boiling point should be sufficiently low to facilitate its removal at the end of the polymerization, should a
totally solvent-free polymer be required.

Co-monomers in the acrylate polymer can contain other functional groups. For example, the hydroxy
45 group may be introduced using 1- or 2-hydroxyethyl acrylate or 3-hydroxypropyl acrylate. Other suitable
functional monomers are: acrylonitrile, 2-(1-aziridinylethyl) methacrylate, carboxyethyl acrylate, acrylamide
and caprolactone acrylate.

Initiators suitable for preparing the acrylates are peroxides and azo-type initiators.

It can be advantageous to choose an initiator which introduces a terminal functional group into the
50 polymer, such as 3-hydroxy-1,1-dimethylbutyl peroxyneohexanoate or 1,1-dimethyl-hydroxybutylperoxy-2-
ethylhexanoate.

The polymerization can also be carried out by group transfer initiation, which permits the introduction of
acrylate end groups into the polymers or the defined placement of acrylic acid groups into the polymer
55 backbone. Such a defined placement permits a control of the subsequent polymer modification, and may
improve the physical properties of the cross-linked product. The terminal acrylate groups make it possible
to increase the molecular weight of the polymer during the photo-polymerization by reaction with reactive acrylate diluents.

When the polymer material is produced in a solvent such as toluene or xylene, these solvents can be subsequently removed by stirring the polymer material under vacuum at 20-150 °C. until a solids level of more than 95% is obtained.

The polyfunctional reagents with which the polymer material is to be modified are mixed into the polymer material and the mixture is stirred at elevated temperatures. The reaction of glycidyl methacrylate with polymer material based on acrylate comonomers is typically carried out at 20-140 °C, over a period of up to about two hours. The treatment of polymer material based on acrylate comonomers with zinc diacrylate is typically carried out under stirring at 60-100 °C.

Preferably acrylates or substituted acrylates, for example, alkyl acrylates may be used as the polyfunctional modifying reagents depending on the desired reaction rate.

It is sometimes advantageous to add these polymer modifiers to the polymer material before other ingredients are added and carry out the chemical polymer modification thermally by heating the polymer material and its modifier at a temperature sufficient to cause a reaction of one of the functional groups on the modifying reagent without significant reaction of a second functional group. The reaction of the second functional group causes cross-linking of the polymer material. Some degree of this cross-linking may be suitable to increase the viscosity of the polymer material.

The polymer modifiers may also be added together with the other ingredients such as the reactive diluent, the cross-linking agent and photo-initiator.

The cure can be achieved on exposure to ultra-violet radiation, for example, low intensity lamps or solar radiation. Solar radiation can be sufficiently effective even behind double glazed windows, provided that the sample thickness is low or the time of exposure is sufficiently long.

The adhesive composition may be formed as a layer or coating at least 1.58 mm (0.0625 inches) thick on a flexible support substrate or carrier. Generally the layer or coating will have a thickness of 1.58 to 12.7 mm (0.0625 to 0.5 inches). The layer or coating is exposed to curing radiation, especially UV radiation having wavelengths between 250 and 400 nm to cure the body of the layer as a resilient shaped body. Surfaces of the layer exposed to oxygen remain uncured and tacky.

The flexible support substrate may serve as a temporary carrier subsequently to be removed to expose a second uncured tacky surface. This second surface may be maintained uncured during its adhesion to the substrate by treatment of the substrate with an oxygen-enriched primer.

The flexible support substrate may also serve as a permanent substrate to which the adhesive layer is securely bonded, for example, a mastic rubber layer.

Instead of employing a separate discrete substrate, the adhesive composition may be blended with a mastic rubber to form a shaped layer in which the adhesive at the surface remains tacky and uncured in the presence of oxygen.

Suitable mastic rubber compositions can be based on butyl rubber, styrene-butadiene copolymers and others or mixtures thereof.

The invention is illustrated by reference to the accompanying drawings which illustrate particular embodiments, in which:

FIGURE 1 is an end cross-section of a strip of the invention which may be rolled or coiled on itself for storage and transport,

FIGURE 2 is a schematic representation of an automobile window bonded with the strip of Figure 1 to an automobile structure.

FIGURE 3 is a representation of another strip product of the invention,

FIGURE 4 is an end cross-section of the strip product of Figure 3 of the invention,

FIGURE 5 is an end cross-section of still another strip product of the invention,

FIGURE 6 is a schematic representation of a double window bonded with the strip of Figures 3 and 4,

FIGURE 7 is a representation similar to that of Figure 6 employing the strip of Figure 5,

FIGURE 8 is a schematic representation of a double window mounted in a frame employing the strip of Figure 1,

FIGURE 9 illustrates schematically an in-line process for producing the strip of Figure 1.

FIGURES 10A, 10B and 10C, illustrate schematically double windows adhesively bonded with different command curb formulations of the invention.
With further reference to Figure 1, a strip 10 comprises an adhesive layer 12 on a support film 14. Adhesive layer 12 has a cured body 16, a tacky outer surface portion 18 and a tacky inner surface portion 20.

Support film 14 has release coatings 22 and 23, for example, a silicone coating on its outer and inner surfaces.

With further reference to Figure 2, a window assembly 24 comprises a glass pane 28 mounted on an automobile structure with an air space 30 therebetween. Opposed inner surfaces of the structure 26 and pane 28 are bonded together adjacent their peripheral edges by the adhesive layer 12 derived from the strip 10 of Figure 1. In mounting such an assembly the tacky surface portion 18 is contacted with peripheral edge of glass pane 28, to bond the tape 10 to pane 28. Thereafter, the support film 14 is removed from adhesive layer 12 to expose tacky surface portion 20, and glass pane 28 with layer 12 thereon is applied in opposed facing relationship with structure 26 and adhered by tacky surface portion 20. The release coating 23 permits ready removal of film 14 from layer 12.

The adherence of tacky surface portions 18 and 20 to the pane 28 and structure 26 respectively results in exclusion of oxygen from the surface portions 18 and 20, whereafter exposure to curing radiation, for example, U.V. radiation passing through pane 28 results in cure of the surface portions 18 and 20 to produce cured contact surfaces 34 and 36 to provide a permanent bond.

In particular, layer 12 is curable by U.V. radiation having wavelengths between 250 and 400 nm and has a thickness of 1.58 to 12.7 mm (0.0625 to 0.5 inches).

With further reference to Figures 3 and 4, a strip 38 includes a rubber layer 40 and an adhesive layer 42 separated by a spacer strip 88 which may be, for example, of metal or plastic. Adhesive layer 42 includes a cured body 44, a tacky outer portion 46, tacky side portions 47 and a cured contact surface 48.

The spacer strip 88 in particular is undulating to provide flexibility to the strip 38. More especially the spacer strip may be a corrugated metal ribbon having spacer side edges. The strip 38 may be employed in bonding glass panes together in a manner analogous to those illustrated in Figures 6 and 7.

With further reference to Figure 5, a strip 50 includes upper and lower rubber layers 52, a spacer 54 and adhesive layers 56. Each adhesive layer 56 includes a cured body 58, an outer tacky surface portion 60 and an inner cured contacting surface 61.

In a variant of Figure 5, the spacer 54 may be omitted and the layers 52 then form a single layer which may consist of plastic, rubber or metal. The single plastic, rubber or metal layer 52 to which the layers 56 are adhered may contain a typical desiccant such as a molecular sieve. In the case of a metal layer 52 the desiccant would be contained in a hollow tube provided with perforations or narrow openings to allow contact between the desiccant and moisture in the air, specifically the gases between two glass panes, as in Figure 7.

With further reference to Figure 6, a window 62 includes glass panes 64 and 66 with an air space 68 therebetween. The panes 64 and 66 are bonded together with strip 38 of Figure 3. In particular, opposed surfaces of the panes 64 and 66 are bonded adjacent their peripheral edges by the tacky side portions 47 of adhesive layer 42. On bonding of the panes 64 and 66 by tacky side portions 47, oxygen is excluded from the side portions 47 and these portions may be cured to produce cured contact sides 70 by curing radiation, for example, ultraviolet radiation passing through glass panes 66 and 64.

With further reference to Figure 7, a window 72 comprises glass panes 74 and 76 separated by an air space 78. The panes 74 and 76 are bonded together adjacent their peripheral edges by the strip 50 of Figure 5. In particular the tacky surface portions 60 of strip 50 are employed to bond the panes 74 and 76 which results in exclusion of oxygen from the surfaces 80 whereafter they are cured to provide the cured contact surfaces 80, for example, by U.V. radiation passing through glass panes 72 and 76.

With further reference to Figure 8, a window 150 comprises glass panes 152 and 154 mounted in a frame 156. Panes 152 and 154 are separated by a spacer 158 and sealed at their peripheral edges by a sealant 160 to define an air space 162 therebetween.

Window 150 is mounted in frame 156 with adhesive layer 12 of strip 10 of Figure 1. Tacky surfaces 18 and 20 of layer 12 are bonded to pane 154 and frame 156 respectively thereby excluding oxygen, whereafter exposure to curing radiation, for example, U.V. radiation passing through window 150 results in cure of surfaces 18 and 20 to provide a permanent bond.

With further reference to Figure 9, there is illustrated an assembly 96 for producing the strip 10 of Figure 1.

Assembly 96 includes a film delivery system 98, an adhesive delivery system 100, a conveyor 102, a curing system 104 and a supplementary curing system 108.

Delivery system 98 comprises rolls 110 and a bath roll 112 for delivering a continuous feed of support film 14 from a source (not shown).
Bath roll 112 is immersed in a bath 114 which suitably contains an oxygen-enriched silane-type primer which is applied to the support film 14. An oxygen line 116 provides a feed of oxygen to the primer in bath 114. The oxygen in the primer serves to inhibit the cure of the adhesive subsequently applied to the film 14.

Adhesive delivery system 100 comprises an extruder die 118 which delivers adhesive in flowable form onto support film 14 as it is conveyed by conveyor 102.

Conveyor 102 comprises a pair of belt rolls 124 and a continuous belt 126 passing about the rolls 124. Support film 14 is supported on belt 126 during application of the adhesive from extruder die 118, whereby an adhesive layer 12 is formed on film 14.

Curing system 104 includes upper and lower banks 120 and 122 of UV lights which direct UV radiation to adhesive layer 12. A continuous belt 126 conveniently has an open surface or is in any event transparent to UV radiation so that such radiation from lower bank 122 may reach adhesive layer 112. For this purpose it is also appropriate that support film 14 be transparent to UV radiation.

Conveniently upper and lower banks 120, 122 are relatively long in length, particularly of the order of 10 metres and comprise low or medium intensity lamps. In this event it is appropriate to employ a supplementary curing system 108 which comprises high intensity upper and lower lamps 128 and 130 with upper and lower lenses 132 and 134 to direct the high intensity radiation.

Spray 136 is optional and applies a primer spray to the finished paper 10 before it is rolled on itself to form the roll 138.

With further reference to Figure 10A, a window assembly 200 comprises spaced apart windows 202 and 204 with an insulating air space 206 therebetween. The windows 202 and 204 are spaced apart by a spacer 208 which may comprise elongated aluminum members of rectangular cross-section. Spacer 208 is bonded to and between the opposed surfaces of windows 202 and 204 by adhesive sealants 210 and 212 initially formed as coatings on opposed sides of spacer 208. The sealants 210 and 212 are derived from capped urethane-forming compositions. After assembling the windows 202 and 204 with the spacer 208 therebetween, coated with the sealants, the assembly 200 is heated to uncap the isocyanates of the composition which therefrom form the sealants 210 and 212.

With further reference to Fig. 10B, a window assembly 220 comprises spaced apart windows 222 and 224 with an insulating air space 226 therebetween. The windows 222 and 224 are separated by a strip 228. Strip 228 comprises a rubber strip 230 with a corrugated spacer strip 232 extending between opposed sides. Neoprene layers 234 are bonded to the opposed sides of the rubber strip 230.

After assembling the windows 222 and 224 with strip 228 therebetween, the assembly is heated to melt the surfaces of the neoprene layers 234 contacting the window surfaces, thereafter the neoprene layers 234 cool to provide a firm adhesive bond.

With further reference to Figure 10C, a window assembly 240 comprises spaced apart windows 242 and 244 with an insulating space 246 therebetween. The windows 242 and 244 are spaced apart by an extruded neoprene strip 246. The adhesive bond between the strip 246 and the windows 242 and 244 is produced in the same manner as described for the neoprene layers 234 in Figure 10B.

The following Examples illustrate the invention in particular and preferred embodiments.

EXAMPLES

A) Materials

The following starting materials were used for the production of the reactive ingredients:

Polyether Diol was grade POLY-G2® of Olin Chemical Company, U.S.A. It has an average molecular weight of 775.

Polyether polyol was grade PLURACOL® 220 obtained from Wyandotte Chemicals, U.S.A.

Aerosil® was grade 130 from Degussa, Germany. It has an average primary particle size of 16 nanometers.

Isodecylacrylate was obtained from Sartomer Company, U.S.A.

Zinc di- and mono-acrylates were obtained from Sartomer Company, U.S.A. The materials are powders of < 45 μm (which pass through a 325 mesh).

Glycidyl Methacrylate was obtained from Sartomer Company, U.S.A.

2-(1-Aziridinyl) ethylmethacrylate was obtained from Aceto Chemical Company, Inc., U.S.A. The material has a purity of >92% by gas-liquid chromatography.
B) Preparation of Reactive Ingredients

Poly (Alkylene Oxide) Diacrylate

This material was prepared by treating a poly(propylene oxide) diol with toluene diisocyanate and subsequent reaction with hydroxypropyl acrylate.

To 537g of poly(propylene oxide)diol of average molecular weight of 775, was added 109g of toluene, 0.1g of benzoyl chloride and 250g of toluene diisocyanate. The solution was heated at 95-100 °C for a period of 3.5 hr. Then was added 191.2g of hydroxypropyl acrylate and the temperature was kept at 95-100 °C for another 2.5 hr. Finally, 0.114 cm³ of stannous octoate was added and heating continued for another 1 hr.

Poly (Alkylene Oxide) Triacrylate

This material was prepared by treating poly (propylene oxide) triol with methylene-bis-cyclohexylisocyanate and subsequent reaction with hydroxypropyl acrylate.

To 1570g of poly(propylene oxide)triol (Wyandotte Pluracol® 220) of a hydroxy number of 26.88, was added 0.5 ml of a 10% solution of tin dibutylaurate in xylene at 70 °C. Then 211g of methylene-bis-cyclohexylisocyanate was added and the temperature increased to 95 °C and kept there for approximately 3 hr. Then another quantity of catalyst was added (0.5 ml) and 104.7g of hydroxypropyl acrylate. The solution was then heated for 4 hr. at 95 °C. Then a third quantity of catalyst was added (0.3 ml), and after 2 hr. of heating, the solution was allowed to cool down. The product had a residual isocyanate content of 0.3%.

C) Acrylate Polymer Production

EXAMPLE 1

Poly(butylacrylate - acrylic acid)

1a) A monomer solution of 588g butylacrylate, 130g of acrylic acid, 1.5g of laurylmercaptan and 1.0g of γ-methacryloxypropyl trimethoxysilane in 50 ml of xylene and a catalyst solution of 20g of laurylperoxide and 4g of t-butylperoxide in 50 ml of xylene were prepared. The polymerization was started with 50 ml of the monomer solution and 2 ml of the catalyst solution by adding to a resin kettle with stirring, with a nitrogen atmosphere and heating to 54 °C. After the induction period was over, the remaining solutions were added in equivalent proportions over 3 hrs. at a reaction temperature of 120-135 °C. The resulting clear polymer was heated for another 3 hours at 100 °C. On cooling, a tough rubbery material, poly(butylacrylate-acrylic acid (84:16) was obtained.

1b) A polymer material was prepared in the manner of Example 1a) employing from 80g butylacrylate, 40g acrylic acid and 0.2g of laurylmercaptan in 10 ml of xylene as the monomer solution and 2g of laurylperoxide and 0.4g of t-butylperbenzoate in 10 ml of xylene as the catalyst solution. The reaction conditions were as for Example 1a). The polymer material is a thermoplastic material poly(butylacrylate-acrylic acid (60:40).

EXAMPLE 2

Poly(ethylacrylate-acrylic acid-acrylonitrile)

a) this polymer material was produced by adding to 320g xylene at 100 °C, the monomer solution and a catalyst solution over a period of 3 hours. The monomer solution contained 2.900g ethyl acrylate, 76g acrylonitrile, 76g acrylic acid and 3g laurylmercaptan. The catalyst solution contained 26g laurylperoxide and 7g butylperbenzoate in 273g of xylene. The material was highly viscous with comonomer proportions of 95:2.5:2.5.
EXAMPLE 3

Poly(butylacrylate-ethylacrylate-acrylonitrile)

This polymer material was produced in the manner of Example 2, except that 1.450g of the ethylacrylate was replaced with 1.450g of butyl acrylate, to produce a polymer of equivalent butyl acrylate and ethylacrylate proportions. Also, the monomer solution contained 1.5g of γ-methacryloxypropyl trimethoxysilane. The material was highly viscous with comonomer proportions of 47.5:47.5:2.5:2.5.

EXAMPLE 4

Poly(butylacrylate-ethylacrylate-acrylic acid)

Into a reaction vessel was added a solution of 72.6g of ethylacrylate, 93g of butylacrylate, 3.8g of acrylic acid, 5g of azo-bis-isobutylisonitrile and 0.68g of lauryl mercapran. Initially, 10g were added and the solution was heated up until the induction period had passed. The main portion was then added at a rate so that the internal temperature remained between 125-130 °C. The addition was carried out over a period of one hour, after which time the polymer material could be stirred easily. The polymer material remains a clear but viscous liquid at 25 °C, with comonomer proportions of 54.5:43.1:2.4.

EXAMPLE 5

Poly(butylacrylate-ethylacrylate-acrylic acid)

Polymerization was initiated with a solution of 21.7g of ethyl acrylate, 50g of butyl acrylate, 3g of acrylic acid, 2g of azo-bis-isobutylisonitrile and 0.2g of lauryl mercapran in a reactor by slow heating, starting at 25 °C. The polymerization started vigorously at 55 °C. The main part of the polymerization was carried out between 100 and 120 °C by a slow addition of 250g of the same monomer mixture over a period of two hours with external waterbath cooling. Since stirring becomes difficult at this stage, the material was removed from the reactor and heated for two additional hours at 120 °C. The polymer material was highly viscous with comonomer proportions of 67:28:5.

EXAMPLE 6

Poly(butylacrylate-ethylacrylate-acrylic acid)

A starting solution of 45g of ethylacrylate, 45g of butylacrylate, 5g of acrylic acid, 0.5g of azo-bis-isobutylisonitrile and 0.35g of lauryl mercapran was added in 5 portions to a stirred reaction kettle at a kettle temperature of 70 °C. Each portion was only added after an exotherm had indicated that the previous portion had reacted. The reaction was continued over a period of three hours at a temperature between 80 °C and 105 °C. with a solution of 442g of ethylacrylate, 44g of butylacrylate, 44g of acrylic acid, 50g of azo-bis-isobutylisonitrile and 6.1g of lauryl mercapran. Because of the high viscosity of the product, stirring in the reaction vessel becomes difficult. The polymer material was removed from the reactor and heated without stirring for 2 hours at 120 °C. The polymer material was rubbery with comonomer proportions of 47.6:47.6:4.8.

EXAMPLE 7

Poly(butylacrylate-ethylacrylate-acrylic acid)

To 1713g of a monomer mixture consisting of 54.3% of butylacrylate, 42.3% of ethylacrylate and 3.4% of acrylic acid was added 40g (2.5%) of azo-bis-isobutylisonitrile and 6.8g (0.4%) of lauryl mercapran at 22 °C. The solution was cooled to 10 °C. and added dropwise to a stirred and heated reaction vessel with a wall temperature of approximately 70 °C. The reaction started immediately. The addition was continued and the reaction vessel cooled at such a rate that the internal temperature remained between 105 and 135 °C. Near the end of the addition, the stirring of the polymer becomes very difficult with a single-blade stirrer because of a strong Weissenberg effect. The addition was complete after 3 hours. The polymer was then heated for another 3 hours at 80-100 °C. The resulting polymer was a highly viscous material with
comonomer proportions of 54:3:42:3:3.4.

EXAMPLE 8

A solution was prepared consisting of 865g butylacrylate, 535g ethylacrylate, 38g acrylonitrile, 76g of $\beta$-carboxyethylacrylate and 1.5g dodecylmercaptan. A second solution was prepared containing 3.5g t-butyl peroxide, 13.5g lauryl peroxide and 137ml mineral spirits. A stirred resin kettle contained 160ml of mineral spirits and was heated to 100 °C. The monomer and initiator solutions were added dropwise at equivalent proportions over a period of 3 hours at a reaction temperature of 95-125°C. with constant stirring, and some cooling in a water bath. The polymer was allowed to cool down.

GLC analysis shows the following residual monomer concentration:

Butylacrylate = 0, ethylacrylate = 0.5%, acrylonitrile = 0.03%, $\beta$-carboxyethylacrylate = 0.1%.

EXAMPLE 9

A solution of 1700 g butylacrylate, 240 g ethylacrylate, 60 g acrylic acid and 4 g dodecylmercaptan was added dropwise to a pre-heated reactor (~ 100 °C. wall temperature). The reactor was stirred with a single-shaft glass stirrer equipped with a Teflon® blade. At the same time was added 80 g of Lupersol® 531-80M, dropwise at a rate that both monomer and peroxide were always added in the same proportions over the total addition period of 3.5 hours. After the initial addition of approximately 25 ml the reactor vessel was cooled so that the reaction temperature remained between 95 and 110 °C. After 200 ml of monomer addition, 30 ml of toluene was added to improve stirring. Another 30 ml were added after a total of 450 ml monomer, and another 70 ml after 600 ml of monomers. The clear polymer was heated at 70 °C. for six hours.

EXAMPLE 10

A four-necked flask, equipped with thermometer, heavy-duty single-shaft glass stirrer containing a Teflon® blade, thermometer, dropping funnels for monomers and initiator solution, and containing 50 g of toluene was heated to cause refluxing of the toluene. The monomer mixture consisted of 1700 g butylacrylate, 240 g ethylacrylate, 60 g acrylic acid and 6 g of dodecylmercaptan. The initiator solution contained 54 g of lauryl peroxide and 14 g t-butylperbenzoate in 150 ml toluene. Over a period of 3 hours the two solutions were added at the equivalent rate into the reactor vessel under stirring and cooling to maintain the reaction between 85 °C and 110 °C. The polymer could easily be stirred. It was heated over night at 70 °C. and then had a viscosity of 23,600 mPas (cps) at 70 °C. (Brookfield, Spindle #3). After 4 hours at 93 °C (200 °F), under vacuum in the Baker/Perkin mixer the solids level was 99.5%. The viscosity at 29 °C. was 2.5 x 10⁶ mPas (cps) and at 70 °C. 0.12 x 10⁴ mPas (cps).

D. Adhesive Compositions

EXAMPLE 11

Surface Treatment of a Compounded Rubber with a Photo-Curable Formulation

A coating of the photo-curable formulation A, in Table I below, of about 0.5 mm thickness was applied to both sides of a strip of compounded rubber. The rubber formulation consisted of 16% butyl rubber, 28% hydrocarbon resins, 21% plasticizer and 37% carbon black and inorganic fillers. The strip was placed between glass plates and both sides of the glass were exposed to low-intensity ultra-violet light of an intensity of 1200 μW/cm². The use of the photo-curable formulation prevented adhesive failure when the glass plates were removed under force or on impact at -34 °C.

EXAMPLE 12

Preparation of a Photo-Cured Adhesive Material in Low-Intensity Ultra-Violet Light

A 0.3 mm thick layer of the photo-curable formulation A, in Table I below, was cast on a sheet of silicone-treated release paper and exposed to low intensity ultra-violet light of an intensity of 1200 μW/cm².
After 30 min. exposure the material was cured but both the upper and lower surfaces remained tacky. The material had a SHORE A hardness of 40, an elongation at break of 150%, a tear strength of 1.37 kg/cm (7.7 lb/in), and a tensile strength of 7.5 kg/cm (42 lb/in). The sample remained flexible at -42 °C and showed good adhesion to glass after attaching glass plates to the upper and lower surface of the material and exposing the system to sunlight for 60 minutes at 25 °C.

EXAMPLE 13

Preparation of Photo-Cured Adhesive Material in High-Intensity Ultra-Violet Light.

The photo-curable formulation B, in Table I below, was extruded in strips of 1.5 cm width and 3 mm thickness onto silicone-treated release paper. The strips were passed under a medium-pressure Hanovia® 652-OA 431 UV lamp of an intensity of 0.129 W/m² (200 W/square inch) at a speed of 0.137 m/s (27 feet per minute). This corresponded to an exposure time of the focused light beam of 0.5 seconds. The cured strip can be transferred to glass or other solid surfaces so that it is attached to one or two such surfaces.

After exposing the system to low-intensity UV light sources, including sunlight, the material bonds to the glass interface.

The material remained flexible and tacky at -32 °C, but became brittle at -35 °C. The material showed cohesive failure on anodized aluminum at -36 °C. in a peel test.

EXAMPLE 14

The polymer of formulation C, in Table I below, was prepared by mechanically stirring 23.7% of zinc diacrylate into 475g of the polymer of Example 7 and then heating at 70 °C. for 5 hours with occasional mixing and deaeration for 5 hours and 30 minutes.

The resulting polymer had very low tack, was not gelled, but was opaque.

To the polymer was then added 42.7g poly(alkylene oxide) triacrylate (9 pph) described above and 2.4g (0.5 pph) Irgacure® 184. The material was mixed at 70 °C. and then deaerated which caused considerable frothing. The material had very little tack, was not gelled, had little flow, and adhered sufficiently to release paper.

Tests show that excellent adhesion to glass developed on exposure of the material to "Black Light".

EXAMPLE 15

Preparation of Photo-Cured Adhesive Material in High-Intensity Ultra-Violet Light for Adhesion to Glass and Metals.

The photo-curable material of formulation C, in Table I below, was cast into a sheet of 2 mm thickness onto release paper. The sheet was cured by six passes underneath a HANOVIA® light source of an intensity of 200 W/square inch at a speed of 0.137 m/s (27 feet/min). This corresponds to an exposure time of 3 seconds to the focused light beam. The material showed a SHORE A hardness of 35 and an elongation of 150%. The cured material has sufficient tack on both the upper and the lower surface to adhere very well to solid surface. The material was cut into 1 cm wide strips and placed between the following surfaces:

glass and milled aluminum

glass and anodized aluminum

glass and glass.

After exposing the glass side to sunlight for one hour behind double-glazed windows, excellent adhesion was obtained to all the interfaces, as evidenced by the cohesive failures when the glass or metal surfaces were removed.

A sheet 20.32 cm (8") wide and 0.47 cm (3/16") thick and 30.54 cm (12") long was allowed to flow slowly into release paper at 40 °C, and is then exposed to a Hanovia® lamp of a focus width of 2.54 cm (1"), at a travelling speed of 1.21 m/min (4 feet per minute). The cured sheet was approximately 35 °C. warm and could easily be removed from the release paper on cooling to 25 °C.
The polymer had the following properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>Initial Polymer</th>
<th>After &quot;Black Light&quot; Exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elongation</td>
<td>350, 500%</td>
<td>300%</td>
</tr>
<tr>
<td>Tear Strength</td>
<td>(16.7; 16.0 psi) 1.15; 1.10 bar (55, 50 psi) 2.79; 3.15 bar</td>
<td></td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>(132, 126 psi) 9.10; 6.89 bar (175, 180 psi) 12.06; 12.57 bar</td>
<td></td>
</tr>
<tr>
<td>Colour</td>
<td>Colourless</td>
<td>Pale Yellow</td>
</tr>
<tr>
<td>Hardness</td>
<td>35-40</td>
<td>35-40</td>
</tr>
<tr>
<td>Flexibility at -32°C.</td>
<td>Partially</td>
<td>Partially</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Property</th>
<th>Initial Polymer</th>
<th>After Black Light Exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elongation</td>
<td>350, 500%</td>
<td>125%</td>
</tr>
<tr>
<td>Adhesion</td>
<td></td>
<td>6.68 bar (97 psi)</td>
</tr>
<tr>
<td>Lap Shear</td>
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<tr>
<td>Glass/Glass</td>
<td>1.74 bar (26 psi)*</td>
<td>9.15 bar (131 psi)</td>
</tr>
<tr>
<td>Glass/Anodized Aluminum</td>
<td>2.51 bar (36 psi)*</td>
<td>8.80 bar (126 psi)</td>
</tr>
</tbody>
</table>

NOTE:

* Adhesive failure: surface remains tacky and can be re-adhered.

EXAMPLE 16

Preparation of Photo-Cured Adhesive Material in High Intensity Ultra-Violet Light for Adhesion to Glass and Metals

The photo-curable material of formulation C in Table 1 was cast at about 60°C into a H-bead in accordance with ASTM C 719-79 and photo cured by exposure to sunlight and tested for elongation and adhesion.

The photocured material displayed the same properties as in Example 19.
EXAMPLE 17

To the polymer of Example 3 was added 2.1% zinc diacrylate at 120 °C. with stirring and subsequent heating at 120 °C. for 30 minutes. Vacuum was applied to deaerate the material. Then 15% of poly-(alkyleneoxide)triacrylate and 0.25% of Irgacure® 184 was added with stirring at 80 °C.

The material was then spread on release paper to a thickness of 4 mm. The material had very little flow at ambient temperature, adhered very well to milled aluminum and glass, and could be removed from release paper and cut.

The material was then exposed to a Hanovia® lamp of a focus width of 2.54 cm (1") at a travelling speed of 1.21 m/min (4 feet per minute).

EXAMPLE 18

To the poly(butylacrylate-ethylacrylate-acrylonitrile) of Example 3 was added 2.1% zinc diacrylate at 120 °C. with stirring and subsequent heating at 120 °C. for 30 minutes. Vacuum was applied to deaerate the material. Then 15% of PAO-TA and 0.25% of Irgacure® 184 were added with stirring at 80 °C.

The material was then spread on release paper to a thickness of 4 mm. The material had very little flow at ambient temperature, adhered very well to milled aluminum and glass, and could be removed from release paper and cut.

The material was then exposed to a Hanovia® lamp of a focus width of 2.54 cm (1") at a travelling speed of 1.21 m/min (4 feet per minute).

The material showed a lap shear strength of 5.93 bar (86 p.s.i.) between glass plates after the glass plates had been exposed to sunlight for three days.

Lap shear specimen were exposed to 1000 hour Q-UV exposure at 60 °C. (8 hours UV light and 4 hours condensation cycle) and then showed an average lap shear value of 4.12 bar (59 psi).

EXAMPLE 19

Photo-Curing and Physical Properties of Polymer of Example 3

A sample of formulation D, in Table I below, was spread out on silicone treated paper (release paper) to a thickness of 3.17 mm (1/8 of an inch) and photocured under Black Light for 3 to 15 minutes, respectively.

The test materials showed elongation at failure values of 500%. The lap shear values between glass were in the range of 4.96-5.23 bar (71-75 p.s.i.) after exposure to sunlight for 3 days.

A sample of formulation D, in Table I below, was spread out on silicone treated paper (release paper) to a thickness of 3.17 mm (1/8 of an inch) and photocured under a Hanovia® UV lamp and then placed between glass, exposed to sunlight for 3 days. The resulting lap shear strength was 3.14 to 3.56 bar (45 to 51 p.s.i.), respectively.

EXAMPLE 20

Photo-Curing and Physical Properties of Polymer of Example 10

Formulation E, in Table I below, was prepared by mixing the polymer with zinc monomethacrylate and heating at 70 °C. for 2 hours. The other ingredients were mixed under high shear mixing (Haake-Buchler Torque Rheometer) and then extruded in sheets of 4.76 mm (3/16 inch) thickness and exposed to Black Light of 120 μW/cm² intensity for 3 minutes. The material then showed 200% elongation at failure. Samples placed between glass and exposed to sun for 3 days developed lap shear strength of 6.77 bar (97 p.s.i).

EXAMPLE 21

When the zinc monomethacrylate in Example 21 was replaced with zinc dimethacrylate, the precured polymer also showed an elongation of failure of 200% and, after exposure of a glass lap shear specimen to sun for 3 days, a lap shear value of 6.01 bar (86 p.s.i.).
EXAMPLE 20

Photo-Curing and Physical Properties of Polymer of Example 10

Formulation E, in Table 1 below, was prepared by mixing the polymer with zinc monomethacrylate and heating at 70 °C for 2 hours. The other ingredients were mixed under high shear mixing (Haake-Buchler Torque Rheometer) and then extruded in sheets of 4.76 mm (3/16 inch) thickness and exposed to Black Light of 120 µW/cm² intensity for 3 minutes. The material then showed 200% elongation at failure. Samples placed between glass and exposed to sun for 3 days developed lap shear strength of 6.77 bar (97 p.s.i.).

EXAMPLE 21

When the zinc monomethacrylate in Example 21 was replaced with zinc dimethacrylate, the precured polymer also showed an elongation of failure of 200% and, after exposure of a glass lap shear specimen to sun for 3 days, a lap shear value of 6.01 bar (88 p.s.i.).
TABLE I

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
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<tbody>
<tr>
<td>Polymer (Ex. 3)</td>
<td>100</td>
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<td>IDA</td>
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<td>7.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PAO-TA</td>
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<td>20.6</td>
<td>9</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>PAO-DA</td>
<td>-</td>
<td>20.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AAD</td>
<td>5</td>
<td>8.4</td>
<td>-</td>
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<td>-</td>
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ZDA = zinc diacrylate
ZMA = zinc monomethylacrylate
IDA = isodecylacrylate
PAO-TA = poly(alkylene oxide) triacrylate
PAO-DA = poly(alkylene oxide) diacrylate
AAD = β-carboxyethylacrylate (i.e., acrylic acid dimer)

Photo-initiated cross-linking of adhesive formulations is restricted to materials which are optically clear. However, formulations which contain inorganic fillers, and are thus less expensive, can be cross-linked by thermal initiation, for example, such as direct heat or microwaves. Acrylate formulations have been developed, which can be cured thermally and remain tacky so that the partially cured material can be used as adhesive tape and sheet. The surface tackiness is due to air inhibition of the acrylate polymerization.
Claims

1. A flexible, preformed adhesive strip comprising:
   a flexible substrate and an adhesive layer supported on said substrate,
   said adhesive layer having a shaped body portion and a first outer surface portion remote from said
   substrate,
   said adhesive layer being transparent to curing radiation and having a thickness of up to twice its
   transparent depth and comprising an essentially solvent-free adhesive polymer composition, being
   substantially cured throughout said body portion and uncured at said first outer surface portion, such
   that said first outer surface portion remains tacky,
   said adhesive layer comprising an acrylate polymer with a plurality of pendant side chains
   containing terminal vinyl groups sufficient to provide cross-linking, and a cross-linking agent for said
   polymer, and being curable by UV-radiation in the range from 250 to 450 nm, only while being exposed
   to said curing radiation to produce a cured composition, and having a transparent depth up to 2.54 cm
   (1 inch), the curing of said adhesive polymer composition by said radiation being inhibited by oxygen.

2. A strip according to claim 1, further including a second flexible substrate in adhering contact
   relationship with said outer surface portion, with a tack such that said second substrate is readily
   removable from said adhesive layer.

3. A strip according to claim 1 wherein the terminal vinyl groups are introduced into the acrylate polymer
   via a modifying reagent which is a metal di- or trifunctional acrylate or a metal hydroxy acrylate of
   formula (I):

   \[ \text{(HO)}_m \text{Me}_x \text{A}_n \]  

   in which Me is a metal, A represents an acrylate radical, x is an integer of at least 2, n and m are both
   integers of at least 1 and \( n + m = x \).

4. A strip according to claim 3, wherein said adhesive polymer is an acrylate polymer derived from
   polymerization of at least one acrylate monomer selected from ethyl acrylate, butyl acrylate, 2-
   ethylhexyl acrylate, \( \beta \)-carboxyethyl acrylate, hydroxypropyl acrylate, acrylic acid and acrylonitrile.

5. A strip according to claim 4, wherein said at least one acrylate is copolymerized with said acrylic acid
   and acrylonitrile.

6. A strip according to claim 1, wherein said adhesive layer comprises a second outer surface portion in
   adhering contact relationship with said substrate.

7. A strip according to claim 6, wherein said second outer surface portion is an uncured tacky portion with
   a tack such that said substrate is readily removable from said adhesive layer.

8. A strip according to claims 1 to 6, wherein said adhesive layer has a thickness of 0.16 to 1.27 cm
   (0.0625 to 0.5 inch).

9. A window structure comprising first and second surfaces, at least said first surface comprising a
   transparent pane, said surfaces being in opposed facing relationship and an adhesive layer bonding
   said surface therewith, said adhesive layer comprising a shaped substantially precured body being
   transparent to curing radiation and having a thickness of up to twice its transparent depth and
   comprising an essentially solvent-free adhesive polymer composition according to claim 1.

10. A laminate comprising:
    first and second self-supporting layers in opposed facing relationship and an adhesive layer there-
    between;
    said adhesive layer having a pre-shaped body portion and opposed first and second outer surface
    portions, said outer surface portions being in contacting relationship with said first and second layers
    respectively,
said adhesive layer being transparent to curing radiation and having a thickness of up to twice its transparent depth and comprising an essentially solvent-free adhesive polymer composition according to claim 1.

Patentansprüche

1. Biegsamer vorgeformter Klebestreifen, umfassend ein biegbares Substrat und eine von dem Substrat getragene Klebstoff-Schicht, wobei die Klebstoff-Schicht einen Teil aus einem Formkörper und einen Teil einer ersten äußeren Oberfläche hat, die dem Substrat abgewandt ist, wobei die Klebstoff-Schicht für eine aushärtende Strahlung durchlässig ist und eine Dicke bis zur zweifachen Tiefe ihrer Durchlässigkeit hat und eine im wesentlichen lösungsmittelfreie Klebstoff-Polymer-Zusammensetzung umfaßt, die durch den gesamten Teil aus dem Formkörper hindurch im wesentlichen ausgehärtet und in dem Teil der ersten äußeren Oberfläche nicht ausgehärtet ist, so daß der Teil der ersten äußeren Oberfläche klebrig bleibt,

wobei die Klebstoff-Schicht ein Acrylat-Polymer mit einer Mehrzahl von Seitenketten, die genügend endständige Vinyl-Gruppen enthalten, um eine Vernetzung zu bewirken, und ein Vernetzungsmit für das Polymer umfaßt und mittels UV-Strahlung im Bereich von 250 bis 450 nm nur während der Einwirkung der aushärtenden Strahlung aushärtbar ist, um eine ausgehärtete Zusammensetzung zu erzeugen, und eine Tiefe ihrer Durchlässigkeit bis zu 2,54 cm (1 inch) hat, wobei die Aushärtung der Klebstoff-Zusammensetzung mittels der Strahlung durch Sauerstoff gehemmt wird.


3. Streifen nach Anspruch 1, worin die endständigen Vinyl-Gruppen in das Acrylat-Polymer auf dem Wege über ein Modifizierungsmittel eingeführt werden, das ein di- oder trifunktionelles Metallacrylat oder ein Metallhydroxyacrylat der Formel (I)

\[(\text{HO})_m\text{Me}^+\text{A}_n\]

ist, worin
Me ein Metall ist,
A einen Acrylat-Rest darstellt,
x eine ganze Zahl von wenigstens 2 ist,
n und m beide ganzen Zahlen von wenigstens 1 sind und \(n + m = x\).


5. Streifen nach Anspruch 4, worin das wenigstens eine Acrylat mit der Acrylsäure und dem Acrylnitril copolymerisiert wird.


7. Streifen nach Anspruch 6, worin der Teil der zweiten äußeren Oberfläche ein ungehärteter klebriger Teil mit einer solchen Klebrigkeit ist, daß das Substrat sich von der Klebstoff-Schicht leicht entfernen läßt.

8. Streifen nach den Ansprüchen 1 bis 6, worin die Klebstoff-Schicht eine Dicke von 0,16 bis 1,27 cm (0,0625 bis 0,5 inch) hat.

9. Fenster-Konstruktion, umfassend eine erste Oberfläche und eine zweite Oberfläche, wobei wenigstens die erste Oberfläche eine transparente Scheibe umfaßt, wobei die Oberflächen einander gegenüber
liegen und einander zugewandt sind, und zwischen den Oberflächen eine diese verbindende Klebstoff-
Schicht, wobei die Klebstoff-Schicht einen geformten, im wesentlichen vorgehärterten Körper umfaßt,
der für aushärtende Strahlung durchlässig ist und eine Dicke bis zur zweifachen Tiefe ihrer Durchläs-
sigkeit hat und eine im wesentlichen lösungsmittelfreie Klebstoff-Polymer-Zusammensetzung nach
Anspruch 1 umfaßt.

10. Laminat, umfassend
eine erste selbsttragende Schicht und eine zweite selbsttragende Schicht, die einander gegenüber
liegen und einander zugewandt sind, und eine dazwischenliegende Klebstoff-Schicht,
wobei die Klebstoff-Schicht einen Teil eines vorgeformten Körpers und einander entgegengesetzte
Teile einer ersten äußeren Oberfläche und einer zweiten äußeren Oberfläche hat, wobei die Teile der
äußeren Oberflächen sich im Kontakt mit der ersten bzw. der zweiten Schicht befinden,
wobei die Klebstoff-Schicht für aushärtende Strahlung durchlässig ist und eine Dicke bis zur zweifa-
chen Tiefe ihrer Durchlässigkeit hat und eine im wesentlichen lösungsmittelfreie Klebstoff-Polymer-
Zusammensetzung nach Anspruch 1 umfaßt.

Reivendations

1. Bande adhésive flexible préformée comprenant :
un substrat flexible et une couche adhésive supportée par ledit substrat,
   ladite couche adhésive ayant une partie de corps formée et une première partie de surface externe
elonginée dudit substrat,
   ladite couche adhésive étant transparente à un rayonnement de durcissement, ayant une épaisseur
jusqu’à deux fois sa profondeur transparente et comprenant une composition polymère adhésive
esensiblement exempte de solvant, étant sensiblement dure sur toute ladite partie de corps et non
durcie sur ladite première partie de surface externe en sorte que ladite première partie de surface
externe reste collante,
   ladite couche adhésive comprenant un polymère d’acylate présentant une série de chaînes
latérales pendantes contenant des groupes vinylé terminaux en quantité suffisante pour assurer une
réticulation, et un agent de réticulation pour ledit polymère, et étant durcissable par un rayonnement
ultraviolet de 250 à 450 nm uniquement lorsqu’elle est exposée audit rayonnement de durcissement
pour produire une composition durcie, et ayant une profondeur transparente allant jusqu’à 2,54 cm (1
pouce), le durcissement de ladite composition polymère adhésive par ledit rayonnement étant inhibé
par l’oxygène.

2. Bande selon la revendication 1, comprenant par ailleurs un second substrat flexible en contact
d’adhésion avec ladite partie de surface externe, avec un pouvoir adhésif tel que ledit second substrat
soit aisément enlevable de ladite couche adhésive.

3. Bande selon la revendication 1, dans laquelle les groupes vinylé terminaux sont introduits dans le
polymère d’acylate via un réactif modificateur qui est un acrylate di-ou trifonctionnel métallique ou un
hydroxy acrylate métallique de formule (I):

\[
(\text{HO})_m\text{Me}x_4n \quad (I)
\]

dans laquelle Me est un métal, A représente un radical acrylate, x est un nombre entier d’au moins 2, n
et m sont tous deux des nombres entiers d’au moins 1 et
n + m = x.

4. Bande selon la revendication 1, dans laquelle ledit polymère adhésif est un polymère d’acylate obtenu
par polymérisation d’au moins un monomère d’acylate choisi parmi l’acylate d’éthyle, l’acylate de
butyle, l’acylate de 2-ethylhexyle, l’acylate de bêta-carboxyéthyle, l’acylate d’hydroxypropyle, l’acide
acylique et l’acrylonitrile.

5. Bande selon la revendication 4, dans laquelle ledit acrylate au moins est copolymérisé avec lesdits
acide acrylique et acrylonitrile.
6. Bande selon la revendication 1, dans laquelle ladite couche adhésive comprend une seconde partie de surface externe en contact adhésif avec ledit substrat.

7. Bande selon la revendication 6, dans laquelle ladite seconde partie de surface externe est une partie collante non durcie ayant un pouvoir adhésif tel que ledit substrat soit aisément enlevable de ladite couche adhésive.

8. Bande selon les revendications 1 à 6, dans laquelle ladite couche adhésive a une épaisseur de 0,16 à 1,27 cm (0,0625 à 0,5 pouces).

9. Structure de fenêtre comprenant une première et une seconde surfaces, au moins ladite première surface comprenant un panneau transparent, lesdites surfaces étant en regard l'une de l'autre et une couche adhésive liant lesdites surfaces entre elles, ladite couche adhésive comprenant un corps formé sensiblement préducri, étant transparente à un rayonnement de durcissement, ayant une épaisseur jusqu'à deux fois sa profondeur transparente et comprenant une composition polymère adhésive essentiellement exempte de solvant selon la revendication 1.

10. Stratifié comprenant :
    une première et une seconde couches autoportantes en regard l'une de l'autre et une couche adhésive appliquée entre elles,
    ladite couche adhésive ayant une partie de corps préformée et, une première et une seconde parties de surface externes opposées, lesdites parties de surface externes étant en relation de contact avec lesdites première et seconde couches, respectivement,
    ladite couche adhésive étant transparente à un rayonnement durcissant, ayant une épaisseur jusqu'à deux fois sa profondeur transparente et comprenant une composition polymère adhésive essentiellement exempte de solvant selon la revendication 1.
FIG. 10A. FIG. 10B. FIG. 10C.