

PATENT SPECIFICATION

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(54) BONDING SURFACES WITH A FILM ADHESIVE

(71) We, CIBA-GEIGY AG, a Swiss Body Corporate, of Basle, Switzerland, 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 the preparation of adhesives in film form, commonly called "film adhesives", containing phenol-aldehyde resins, and to their use.

Structural adhesive bonding is a well established procedure in the manufacture of aircraft and in similar industries. Adhesives employed for this purpose are often used in the form of solid films, thereby eliminating difficulties which may occur when a liquid adhesive is used, such as evaporation of a solvent, loss of adhesive from the required site, and uneven distribution. Phenol-aldehyde resins have a high reputation as adhesives and are often required in film form.

Conventionally, film adhesives are prepared either by a technique involving evaporation of a solvent or by extrusion. In the former method, a resin composition is dissolved in a volatile solvent, the solution is poured onto a flat surface, and the solvent is then allowed or caused to evaporate, leaving a film of the composition. In the latter method, the resin composition is heated to its melting point, extruded through a narrow slit, and then cooled or allowed to cool.

Such methods are not always entirely satisfactory. Use of a volatile solvent normally presents toxicity and/or flammability problems, energy must be expended on removing the solvent, and plant for recovering that solvent must be installed if costly wastage is to be avoided. Heating, whether for evaporation of the solvent or for extrusion purposes, often results in advancement of the resin which shortens the shelf life of the film and may lead to a premature gelation of the resin composition. Further, such methods are not suitable for making film adhesives out of resins which are both substantially insoluble in volatile solvents and not readily fusible, such as one in the B-stage or an advanced resin of very high molecular weight. They are also unsuitable for use with compositions in which a latent curing effect is achieved by using discrete particles of a solid resin and discrete particles of a solid hardener, the resin and hardener not reacting together whilst the components are in particulate form but starting to cure as soon as the components are brought into intimate contact by being dissolved in a solvent or by being fused together.

A method has now been found in which there is used a film adhesive which may be prepared from a phenol-aldehyde resin at ambient temperatures without the use of a volatile solvent. It is suitable for resins insoluble in common solvents, for fusible as well as difficultly fusible resins, and also for those resins which react with their hardeners on fusing or on solution in solvents. The method causes little or no advancement of the resin, and the shelf-life of the film adhesive is thus dependent only upon the nature of the resin and the hardener, and not upon the conditions of its manufacture.

In this novel method, a liquid composition containing a phenol-aldehyde resin and a photopolymerisable compound is photopolymerised to form an essentially solid continuous film by exposure to actinic radiation, optionally in the presence of a catalyst for the photopolymerisation, but without thermally crosslinking it; the film so obtained is then used to bond surfaces together by the application of heat and, if desired, pressure. The period of heating can be very short, as there need be no solvent to evaporate and the films need not be thick, typically 20 to 250 μm .

The present invention accordingly provides a method for bonding two surfaces together which comprises

i) exposing to actinic radiation a layer of a liquid composition containing a thermosettable phenol-aldehyde resin, a photopolymerisable compound (other than a phenol-aldehyde resin) and, if required, a heat-curing agent for the phenol-aldehyde resin, until the said composition solidifies to form an essentially solid continuous film due to photopolymerisation of the said photopolymerisable compound while the phenol-aldehyde resin remains substantially in the thermosettable state,

ii) sandwiching between, and in contact with, the two surfaces the film so formed, and

iii) heating the assembly to cure the phenol-aldehyde resin.

There are also provided articles having surfaces bonded by the method of this invention.

Compositions used to prepare the films of the present invention must be liquid under the conditions used in making the films but are preferably solvent-free.

The photopolymerisable component may be of any chemical type known to polymerise under the influence of actinic radiation. Such materials are described in, for example, Kosar, "Light-sensitive Systems: Chemistry and Application of Non-Silver Halide Potographic Processes", Wiley, New York, 1965, 473 pp.

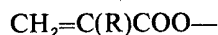
As is well known, such components fall into two main classes

a) those which are polymerised through a free radical chain reaction (photoinitiated polymerisation) and

b) those in which polymerisation is effected by reaction of an excited monomer of the molecule with an unexcited molecule of the monomer.

The first type require only one photopolymerisable group per molecule to form long chains on polymerisation, while the second type must have at least two photopolymerisable groups per molecule, since if they have only one such group per molecule they will dimerise but not polymerise on irradiation.

Photopolymerisable substances of the first type preferred for use in this invention have one ethylenic linkage, or more than one providing they are unconjugated. Examples of these substances are styrene, crotonic acid, and more preferably, acrylic esters containing at least one group of the general formula I, II, or III.



where R is a hydrogen, chlorine, or bromine atom, or an alkyl hydrocarbon group of 1 to 4 carbon atoms, especially a hydrogen atom or a methyl group. More specific examples of the preferred acrylic esters are neopentyl glycol diacrylate and the esters of any of formulae XV to XIX below.

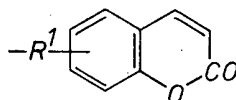
Photopolymerisable materials of the second type include those having at least two, and preferably three or more, groups which are azido, coumarin, stilbene, maleimide, pyridinone, chalcone, propenone, or pentadienone, or acrylic acid groups which are substituted in their 3-position by groups having ethylenic unsaturation or aromaticity in conjugation with the ethylenic double bond of the acrylic group.

Examples of suitable azides are those containing at least two groups of the formula



where AR denotes a mononuclear or dinuclear divalent aromatic radical containing from 6 to 14 carbon atoms, especially a phenylene or naphthylene group.

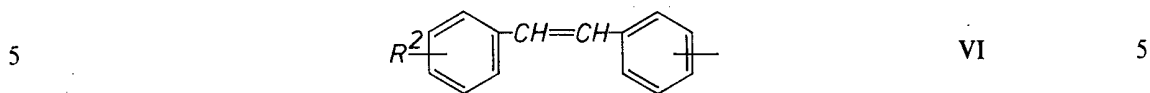
Examples of suitable coumarins are those containing at least two groups of the formula



V

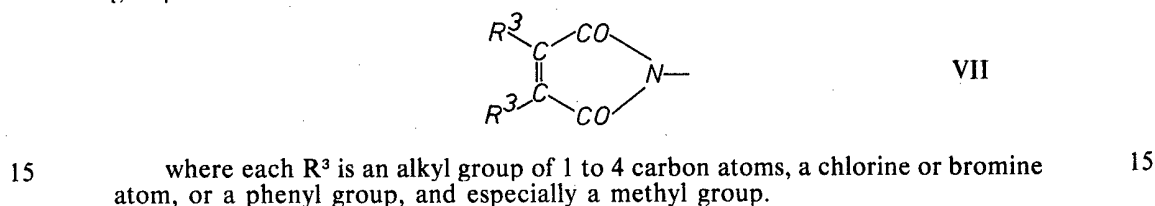
where R^1 is an oxygen atom, a carbonyloxy group ($-\text{COO}-$), a sulphonyl group, or a sulphonyloxy group.

Examples of those containing stilbene groups are those containing at least two groups of the formula

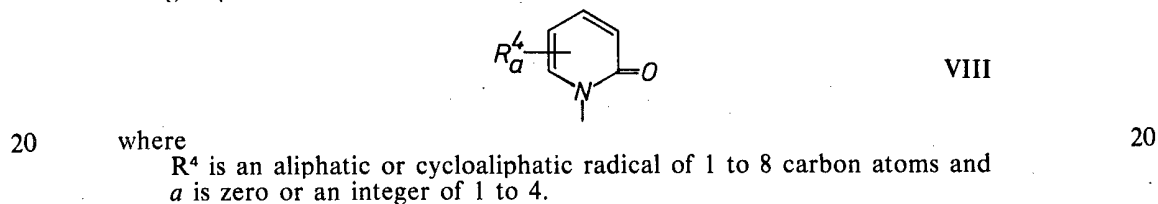


10 where R^2 is the residue, containing up to 8 carbon atoms in all, of a five or six-membered nitrogen-containing heterocyclic ring fused to a benzene or naphthalene nucleus and linked through a carbon atom of the said heterocyclic ring adjacent to a nitrogen hetero atom thereof to the indicated benzene nucleus, such as a benzimidazolyl, benzoxazolyl, benzotriazolyl, benzothiazolyl, or a naphtotriazolyl group. 10

Examples of those containing maleimide units are those having at least two groups of the formula

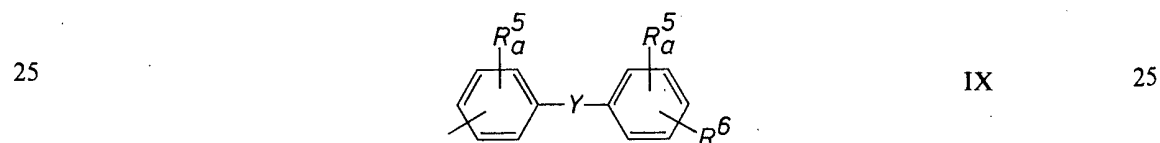


Examples of those containing pyridinone units are those containing at least two groups of the formula

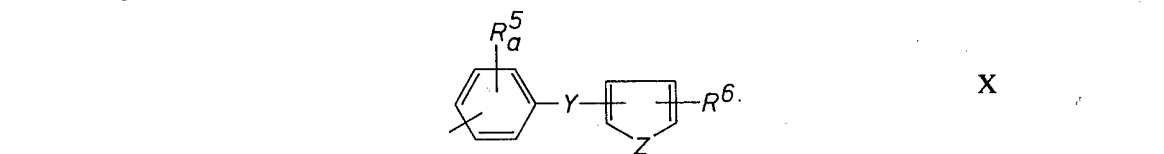


R^4 is an aliphatic or cycloaliphatic radical of 1 to 8 carbon atoms and a is zero or an integer of 1 to 4.

Examples of compounds containing chalcone, propenone, and pentadienone groups are those containing at least two groups of the formula

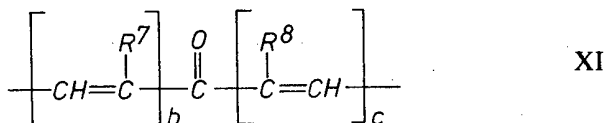


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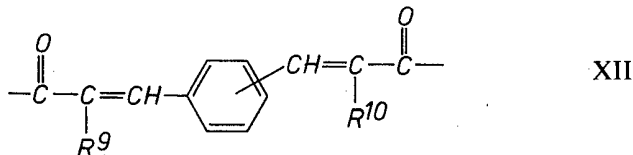


30 where each R^5 is a halogen atom, or an alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkoxy, cycloalkoxy, alkenoxy, cycloalkenoxy, carbalkoxy, carbocycloalkoxy, carbalkenoxy, or carbocycloalkenoxy group, such organic groups containing 1 to 9 carbon atoms, or is a nitro group, or a carboxyl, sulphonic, or phosphoric acid group in the form of a salt, 30

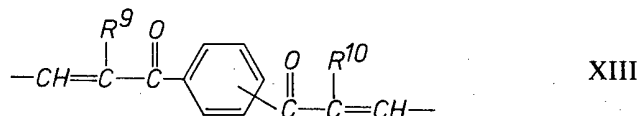
35 a has the meaning previously assigned, R^6 represents a valency bond or a hydrogen atom, Y represents a grouping of formula 35



or



or



5 R^7 and R^8 are each individually a hydrogen atom, an alkyl group of 1 to 4 carbon atoms, or an aryl group, preferably a mononuclear group such as a phenyl group, or R^7 and R^8 conjointly denote a polymethylene chain of 2 to 4 methylene groups, 5

10 R^9 and R^{10} are each a hydrogen atom, an alkyl group of 1 to 4 carbon atoms, or an aryl group, preferably a mononuclear group such as a phenyl group, b and c are each zero, 1, or 2, with the proviso that they are not both zero, and Z is an oxygen or sulphur atom. 10

Suitable 3-substituted acrylates are those containing at least two groups of the general formula



15 where 15

R^{11} is an aliphatic or mononuclear aromatic, araliphatic, or heterocyclyl group, preferably of up to 12 carbon atoms, having, as already indicated, ethylenic unsaturation or aromaticity in conjugation with the double bond shown, such as a prop-2-enyl, phenyl, 2-furyl, 2- or 3-pyridyl, or styryl group, and

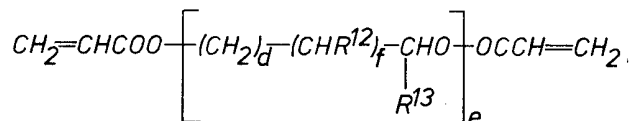
20 R has the meaning previously assigned. 20

Specific examples are diacrylates of poly(oxyethylene) glycols and poly(oxypropylene) glycols.

If desired, a mixture of photopolymerisable compounds may be used.

25 Especially preferred photopolymerisable components used in the process of this invention are, as already mentioned, neopentyl glycol diacrylate and esters of acrylic acid which are of any of the following general formulae XV to XIX. 25

Formula XV is



where

30 d is an integer of 1 to 8, 30

e is an integer of 1 to 20,

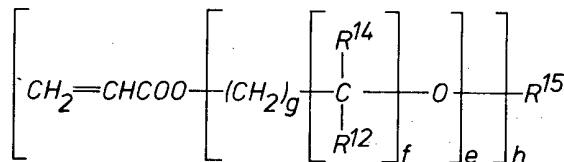
f is zero or 1,

R^{12} denotes $-\text{H}$, $-\text{OH}$, or $-\text{OOCCH}=\text{CH}_2$, and

35 R^{13} denotes $-\text{H}$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{CH}_2\text{OH}$, or $-\text{CH}_2\text{OOCCH}=\text{CH}_2$. 35

Examples of compounds of formula XV are triethylene glycol diacrylate and tetraethylene glycol diacrylate.

Formula XVI is



where

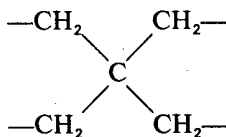
40 e , f , and R^{12} have the meanings assigned above, 40

g is zero or a positive integer, preferably of not more than 8, provided that f and g are not both zero,

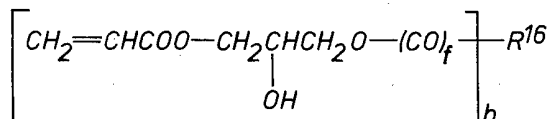
h is 1, 2, 3, or 4,

R^{14} denotes $-\text{H}$, $-\text{Cl}$, $-\text{CH}_3$, or $-\text{C}_2\text{H}_5$, and

R^{15} denotes an organic radical of valency h , linked through a carbon atom or carbon atoms thereof to the indicated h terminal oxygen atom or atoms, preferably the hydrocarbon residue of an aliphatic alcohol containing from 1 to 6 carbon atoms, such as $-\text{CH}_3$ or



A specific example is 2-methoxyethyl acrylate.
Formula XVII is



where

f and h have the meanings previously assigned and

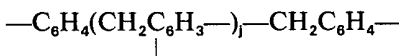
R^{16} denotes an organic radical of valency h , linked through a carbon atom thereof, other than the carbon atom of a carbonyl group.

More particularly, when f is zero, R^{16} may denote the residue, containing from 1 to 18 carbon atoms, of an alcohol or phenol having h hydroxyl groups.

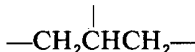
R^{16} may thus represent, for example

either an aromatic group (which may be substituted in the ring by alkyl groups), an araliphatic, cycloaliphatic, heterocyclic, or heterocycloaliphatic group, such as an aromatic group containing only one benzene ring, optionally substituted by chlorine or by one or more alkyl groups each of from 1 to 9 carbon atoms, or an aromatic group comprising a chain of two benzene rings, optionally interrupted by an ether oxygen atom, an aliphatic hydrocarbon group of 1 to 4 carbon atoms, or a sulphone group, each benzene ring being optionally substituted by one or more chlorine atoms or by one or more alkyl groups each of from 1 to 6 carbon atoms, or, preferably, a saturated or unsaturated, straight or branched-chain aliphatic group, which may contain one or more ether oxygen linkages and which may be substituted by one or more hydroxyl groups, especially a saturated or monoethylenically-unsaturated straight chain aliphatic hydrocarbon group of from 1 to 8 carbon atoms.

Specific examples of such groups are the aromatic groups of the formulae $-\text{C}_6\text{H}_5$ and $-\text{C}_6\text{H}_4\text{CH}_3$, in which case h is 1; $-\text{C}_6\text{H}_4\text{C}(\text{CH}_2)_2\text{C}_6\text{H}_4-$, and $-\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4-$, in which case h is 2, and



where j is 1 or 2, in which case h is 3 or 4, and the aliphatic groups of formula



or



in which case h is 3, of formula $-(\text{CH}_2)_4-$, $-\text{CH}_2\text{CH}=\text{CHCH}_2-$, $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$, or $-(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2\text{CH}_2-$, in which case h is 2, or of the formula $-(\text{CH}_2)_3\text{CH}_3$, $-(\text{CH}_2)_4\text{OH}$, $-\text{CH}_2\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_2\text{OH}$, $-\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$, or $-\text{CH}_2\text{CH}=\text{CHCH}_2\text{OH}$, in which case h is 1.

When f is 1, R^{16} may represent the residue, containing from 1 to 60 carbon atoms, of an acid having h carboxyl groups, preferably a saturated or ethylenically-unsaturated, straight chain or branched aliphatic hydrocarbon group of from 1 to 20 carbon atoms, which may be substituted by one or more chlorine atoms and which may be interrupted by one or more ether oxygen atoms and/or by one or more carbonyloxy groups, or a saturated or ethylenically-unsaturated cycloaliphatic or aliphatic-cycloaliphatic hydrocarbon group of at least 4 carbon atoms, which may be substituted by one or more chlorine atoms, or

an aromatic hydrocarbon group of from 6 to 12 carbon atoms, which may be substituted by one or more chlorine atoms.

Further preferred are such compounds in which R¹⁶ represents a saturated or ethylenically-unsaturated straight chain or branched aliphatic hydrocarbon group of from 1 to 8 carbon atoms, optionally substituted by a hydroxyl group, or

a saturated or ethylenically-unsaturated straight chain or branched aliphatic hydrocarbon group of from 4 to 50 carbon atoms and interrupted in the chain by one or more carbonyloxy groups, or

a saturated or ethylenically-unsaturated monocyclic or dicyclic cycloaliphatic hydrocarbon group of 6 to 8 carbon atoms, or

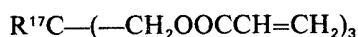
an ethylenically-unsaturated cycloaliphatic-aliphatic hydrocarbon group of from 10 to 51 carbon atoms, or

a mononuclear aromatic hydrocarbon group of from 6 to 8 carbon atoms.

Specific examples of these residues of carboxylic acids are those of the formula —CH₃, —CH₂CH₃, —CH₂CH(OH)CH₃, —CH₂Cl, and —C₆H₅, in which case *h* is 1, and —CH₂CH₂—, —CH=CH—, and —C₆H₄—, in which case *h* is 2.

Specific examples of suitable compounds of formula XVII are 1,4 - bis(2 - hydroxy - 3 - (acryloxy)propoxy)butane, a poly(2 - hydroxy - 3 - (acryloxy)propyl)ether of a phenol-formaldehyde novolak, 1 - (2 - hydroxy - 3 - acryloxypropoxy) - butane, - *n* - octane, and - *n* - decane, bis (2 - hydroxy - 3 - acryloxypropyl) adipate, 2 - hydroxy - 3 - acryloxypropyl propionate, and 3 - phenoxy - 2 - hydroxypropyl acrylate.

Formula XVIII is



where R¹⁷ denotes CH₃—, C₂H₅—, or CH₂=CHCOOCH₂—.

Examples of such acrylates are pentaerythritol tetra-acrylate and 1,1,1-trimethylolpropane triacrylate.

Formula XIX is



where R¹⁸ denotes either an alkyl group of 1 to 6 carbon atoms, optionally substituted by one hydroxyl group, such as an ethyl, *n*-propyl, *n*-butyl, 2-hydroxyethyl, or 2-hydroxypropyl group, or a dialkylaminoalkyl group containing in all 3 to 12 carbon atoms, such as a diethylaminoethyl group.

Phenol-aldehyde resins used in accordance with the present invention may be any resol or novolak prepared from a phenol and an aldehyde under acid or alkaline conditions. Suitable phenols include phenol itself, resorcinol, alkyl-substituted phenols, such as cresols, xylenols, and tertiary butyl phenols, and aryl-substituted phenols, especially *p*-phenylphenol. The aldehyde which is condensed with the phenol is preferably formaldehyde but other aldehydes such as acetaldehyde and furfuraldehyde may also be used. Preferred phenol-aldehyde resins are those made from phenol itself and formaldehyde.

The molar ratio of photopolymerisable component to phenol-aldehyde resin in the compositions is generally from 1:10 to 10:1, ratios from 1:5 to 5:1 being preferred.

Preferably the photopolymerisable component is irradiated in the presence of a photopolymerisation catalyst therefor.

Photopolymerisation catalysts suitable for use in the present invention are well known and are readily found by routine experimentation. They are described in, for example, the book by Kosar cited above: the catalyst must not, of course, give rise to a substantial degree of photoinduced polymerisation through consumption of crosslinking groups or sites in the phenol-aldehyde resin; further, the photopolymerisation catalyst must not cause curing of the phenol-aldehyde resin to a substantial extent. The catalysts fall into two main classes—

(a) those which, on irradiation, give an excited state that leads to the formation of free radicals which then initiate polymerisation of the monomer (photoinitiators) and

(b) those which, on irradiation, give an excited state which in turn transfers its energy to a molecule of the monomer, giving rise to an excited molecule of the monomer which then crosslinks with an unexcited molecule of the monomer (photosensitisers).

The first class includes organic peroxides and hydroperoxides, α -halogen

substituted acetophenones such as 2,2,2-trichloro-4'-*tert.* butylacetophenone, benzoin and its alkyl ethers, e.g., the *n*-butyl ether, α -methylbenzoin, benzophenones, *O*-alkoxycarbonyl derivatives of an oxime of either benzil or 1-phenylpropane-1,2-dione, such as benzil (*O*-ethoxycarbonyl)- α -monoxime and 1-phenylpropane-1,2-dione-2-(*O*-ethoxycarbonyl)oxime, benzil acetals, e.g., its dimethyl acetal, anthraquinones, and photoredox systems comprising a mixture of a phenothiazine dye (e.g., methylene blue) or a quinoxaline (e.g., a metal salt of 2-(*m*- or *p*-methoxyphenyl)quinoxaline-6'- or 7'-sulphonic acid) with an electron donor such as benzenesulphinic acid or other sulphinic acid or a salt thereof, an arsine, a phosphine, or thiourea, these initiators being used with photopolymerisable compounds of the first type, especially those containing at least one group of the general formula I, II, or III.

The photosensitisers include 5-nitroacenaphthene, 4-nitroaniline, 2,4,7-trinitro-9-fluorenone, 3-methyl-1,3-diaza-1,9-benzanthrone, and bis(dialkylamino)benzophenones, especially Michler's ketone, i.e., bis(*p*-dimethylamino)benzophenone.

Generally, 0.1 to 20%, and preferably 0.5 to 10% by weight, of the photopolymerisation catalyst is incorporated, based on the weight of the photopolymerisable compound.

In the photopolymerising step actinic radiation of wavelength 200–600 nm is preferably used. Suitable sources of actinic radiation include carbon arcs, mercury vapour arcs, fluorescent lamps with phosphors emitting ultraviolet light, argon and xenon glow lamps, tungsten lamps, and photographic flood lamps. Of these, mercury vapour arcs, particularly sun lamps, fluorescent sun lamps, and metal halide lamps are most suitable. The time required for the exposure of the photopolymerisable component will depend upon a variety of factors which include, for example, the individual substance used, the proportion of that substance in the composition, the type of light source, and its distance from the composition. Suitable times may readily be determined by those familiar with photopolymerisation techniques, but the product so photopolymerised must still be curable by heating. Of course, irradiation is carried out at a temperature below that at which substantial heat-curing would occur.

Phenol-aldehyde novolaks are used with, as heat-curing agent, a substance liberating formaldehyde under the action of heat, such as paraform but usually hexamethylenetetramine. Resols may, if desired, be applied with, as heat-curing agent, a latent acid catalyst. The heat-curing agent is usually dissolved or suspended in the liquid composition before irradiation. The temperatures, the duration of heating, and the amount of formaldehyde-liberator or latent acid catalyst required for thermal curing, i.e., for bonding the two surfaces together, are readily found by routine experimentation and easily derivable by those skilled in the art from what is already well known concerning the heat-curing of phenolic resins.

The film may be provided with a carrier or a strippable backing sheet, e.g. of a polyolefin, a nylon (i.e., an aliphatic polyamide), or a polyester, or of cellulose paper having a coating of a silicone as release agent, which is removed before the film is sandwiched between the surfaces to be bonded. Manipulation of the assembly is often easier if the film has a tacky surface. This may be produced by coating the film with a substance which is tacky at room temperature but which cures to a hard, insoluble, infusible resin under the conditions of heat employed to cure the phenol-aldehyde resin component of the film. However, an adequate degree of tackiness often exists without additional treatment, especially if the phenol-aldehyde resin in the film is not too far advanced.

Suitable adherends include metals such as aluminium and stainless steel, glass, ceramics, and wood.

The following Examples illustrate the invention. Temperatures are in degrees Celsius and, unless otherwise indicated, parts are by weight. All lap shear strengths quoted are the mean of five results and were determined by British Ministry of Aviation, Aircraft Materials Specification DTD 5577, November 1965. "Solids content" means "resin-forming content" i.e., the percentage by weight left as residue after a 1 g sample of the material has been heated in a 5 cm diameter dish in an oven at 120° for 3 hours at atmospheric pressure.

Materials used in the Examples were the following:

Phenolic Resin I

denotes a liquid phenol-formaldehyde resol in which the phenol:

formaldehyde molar ratio was 1:1.43 and having a solids content of 90%. The number average molecular weight was 240.

Phenolic Resin II

denotes a solid phenol-formaldehyde novolak of number average molecular weight 420 and a phenol:formaldehyde molar ratio of 1:0.72.

Phenolic Resin III

denotes a liquid phenol-formaldehyde resol in which the phenol:formaldehyde molar ratio was 1:1.6 and having a solids content of 82%. Its number average molecular weight was 283.

Acrylate A

This denotes neopentyl glycol diacrylate.

Acrylate B

This denotes 1,1,1-trimethylolpropane triacrylate.

Acrylate C

Phenyl glycidyl ether of epoxide content 6.13 equiv./kg (100 g), 0.3 g of tetramethylammonium chloride, and 0.2 g of hydroquinone were stirred at 120° and 44.1 g of acrylic acid (1 equiv. per epoxide equiv.) was added over 15 minutes. The mixture was stirred at 120° for a further hour, by which time its epoxide content had fallen from its initial value of 4.26 to 0.9 equiv./kg to furnish Acrylate C, i.e., substantially 3 - phenoxy - 2 - hydroxypropyl acrylate.

Acrylate D

n-Butyl glycidyl ether of epoxide content 7.59 equiv./kg (500 g), 1.5 g of tetramethylammonium chloride, and 1.55 g of 2,6 - di - *tert*.butyl - *p* - cresol were stirred together at 100°, and 273.3 g of acrylic acid (1 equiv. per epoxide equiv.) was added over 1 hour. The mixture was stirred at 100° for a further 6 hours, by which time its epoxide content had fallen to 0.83 equiv./kg. The product, Acrylate D, is substantially 3 - *n* - butoxy - 2 - hydroxypropyl acrylate.

Sorbate A

To a stirred mixture of 100 g of a poly(oxyethylene)glycol (average molecular weight 200), 110 g of triethylamine, and 50 ml of toluene at room temperature was added 130.5 g of sorboyl chloride over 30 minutes. The mixture was stirred at 80° for 1 hour, cooled to room temperature, and then filtered, and the solvent was distilled off under reduced pressure to leave the desired poly(oxyethylene) disorbate.

EXAMPLE 1

A liquid composition was prepared containing Phenolic resin I (50 parts), Acrylate A (50 parts), and benzil dimethyl acetyl (1 part). This composition contained 1.26 moles of the acrylate per mole of the phenolic resin.

This composition was applied as a coating onto siliconised paper at room temperature to give a film thickness of 36 μm . The film was irradiated using a 400 w metal halide-quartz lamp, emitting predominantly in the 365 nm waveband, at a distance of 30 cm for 30 seconds.

The film was peeled off the paper, cut to size, and sandwiched between two "Alclad 3L 73" aluminium alloy sheets that had been degreased in trichloroethylene and pickled in chromic acid solution ("Alclad" is a Registered Trade Mark). Overlap joints (1.27 cm) were prepared by pressing the assembly under a pressure of 340 kN/m² for 1 hour at 150°. The lap shear strength of the joints was 5.73 MN/m².

EXAMPLE 2

Example 1 was repeated, using a liquid composition prepared from Phenolic resin I (70 parts), Acrylate B (30 parts), and benzoin *n* - butyl ether (1 part). i.e., 0.38 mole of Acrylate B per mole of the phenolic resin. The lap shear strength of the joints was 6.66 MN/m².

EXAMPLE 3

Example I was repeated, using a liquid composition prepared from Phenolic

resin I (30 parts), Acrylate C (70 parts), and benzil dimethyl acetal (1 part), i.e., approximately 3 moles of the acrylate per mole of the phenolic resin, but the film was irradiated for 60 seconds. The lap shear strength of the joints was 4.35 MN/m².

EXAMPLE 4

Example 1 was repeated, using a liquid composition prepared from Phenolic resin II (70 parts), Acrylate A (30 parts), benzil dimethyl acetal (1 part), and hexamethylene tetramine (4 parts), i.e. containing 0.84 mole of the acrylate per mole of the phenolic resin. The film was irradiated for 60 seconds. The lap shear strength was 1.64 MN/m².

EXAMPLE 5

Example 1, was repeated, using a liquid composition prepared from Phenolic resin III (70 parts), Acrylate C (30 parts), and benzil dimethyl acetal (1 part). The lap shear strength was 10.65 MN/m².

EXAMPLE 6

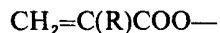
Example 1 was repeated, using a liquid composition prepared from Phenolic resin III (70 parts), Sorbate A (30 parts), and Michler's ketone (1 part). The film was irradiated for 120 seconds, and the lap shear strength of the joint obtained was 8.77 MN/m².

EXAMPLE 7

The procedure of Example 1 was repeated with a liquid composition comprising Phenolic resin I (70 parts), Acrylate D (30 parts), and benzil dimethyl acetal (1 part), except that the composition was applied as a coating 75 μm thick onto a nylon carrier. The lap shear strength of the joints was 9.7 MN/m².

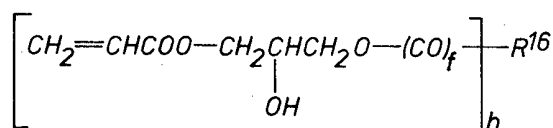
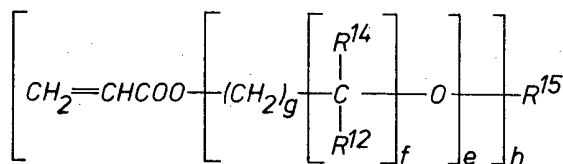
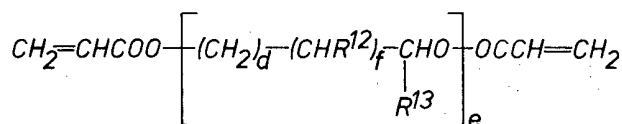
WHAT WE CLAIM IS:—

1. A method for bonding two surfaces together which comprises
 - i) exposing to actinic radiation a layer of a liquid composition containing a thermosettable phenol-aldehyde resin and a photopolymerisable compound (other than a phenol-aldehyde resin) until the composition solidifies to form an essentially solid continuous film due to photopolymerisation of the said photopolymerisable compound while the phenol-aldehyde resin remains substantially in the thermosettable state,
 - ii) sandwiching between, and in contact with, the two surfaces the film so formed and
 - iii) heating the assembly to cure the phenol-aldehyde resin.
2. A method according to Claim 1, in which the composition contains a heat-curing agent for the phenol-aldehyde resin.
3. A method according to Claim 1 or 2, in which the molar ratio of phenol-aldehyde resin to photopolymerisable compound is from 10:1 to 1:10.
4. A method according to Claim 3, in which the said molar ratio is from 5:1 to 1:5.
5. A method according to any preceding claim, in which the phenol-aldehyde resin is a resol or novolak prepared from phenol itself, resorcinol, an alkyl-substituted phenol, or an aryl-substituted phenol.
6. A method according to any preceding claim, in which the phenol-aldehyde resin is one made from formaldehyde.
7. A method according to any preceding claim, in which the photopolymerisable compound is photopolymerised through a free-radical chain reaction.
8. A method according to Claim 7, in which the photopolymerisable component has one ethylenic linkage, or, providing they are unconjugated, more than one.
9. A method according to Claim 8, in which the photopolymerisable component is an acrylic ester containing at least one group of formula



where R is a hydrogen, chlorine, or bromine atom, or an alkyl hydrocarbon group of 1 to 4 carbon atoms.

10. A method according to Claim 9, in which the acrylic ester is neopentyl glycol diacrylate or of one of the formulae.



and



where

R¹² denotes —H, —OH, or —OOCCH=CH₂,

R¹³ denotes —H, —CH₃, —C₂H₅, —CH₂OH, or —CH₂OOCCH=CH₂,

R¹⁴ denotes —H, —Cl, —CH₃, or —C₂H₅,

R¹⁵ denotes an organic radical of valency *h*, linked through a carbon atom or carbon atoms thereof to the indicated *h* terminal oxygen atom or atoms,

R¹⁶ denotes an organic radical of valency *h*, linked through a carbon atom thereof, other than the carbon atom of a carbonyl group,

R¹⁷ denotes CH₃—, C₂H₅—, or CH₂=CHCOOCH₂—,

R¹⁸ denotes either an alkyl group of 1 to 6 carbon atoms, optionally substituted by one hydroxyl group, or a dialkylaminoalkyl group containing in all 3 to 12 carbon atoms,

d is an integer of from 1 to 8,

e is an integer of from 1 to 20.

f is zero or 1,

g is zero or a positive integer, providing that *f* and *g* are not both zero, and

h is 1, 2, 3, or 4.

11. A method according to any of Claims 1 to 6, in which the photopolymerisable compound is photopolymerised by reaction of an excited molecule of the monomer with an unexcited molecule of the monomer.

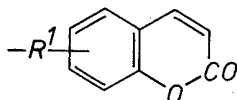
12. A method according to Claim 11, in which the photopolymerisable compound has at least two groups which are azido, coumarin, stilbene, maleimide, pyridinone, chalcone, propenone, pentadienone, or acrylic acid groups which are substituted in their 3-position by groups having ethylenic unsaturation or aromaticity in conjugation with the ethylenic double bond of the acrylic group.

13. A method according to Claim 12, in which the photopolymerisable compound contains at least two groups of the formula



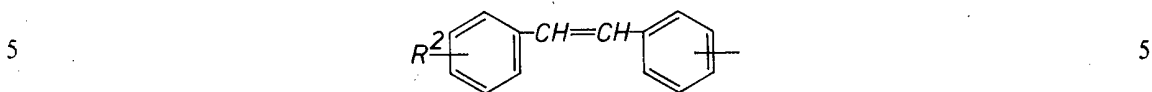
where Ar denotes a mononuclear or dinuclear divalent aromatic radical containing from 6 to 14 carbon atoms.

14. A method according to Claim 12, in which the photopolymerisable compound contains at least two groups of the formula



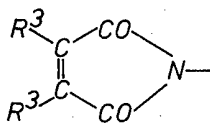
where R^1 is an oxygen atom, a carbonyloxy group ($-\text{COO}-$), a sulphonyl group, or a sulphonyloxy group.

15. A method according to Claim 12, in which the photopolymerisable compound contains at least two groups of the formula



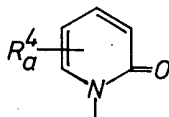
where R^2 is the residue, containing up to 8 carbon atoms in all, of a five or six-membered nitrogen-containing heterocyclic ring, fused to a benzene or naphthalene nucleus, and linked through a carbon atom of the said heterocyclic ring adjacent to a nitrogen hetero atom thereof to the indicated benzene nucleus.

10 16. A method according to Claim 12, in which the photopolymerisable compound contains at least two groups of the formula 10



where each R^3 is an alkyl group of 1 to 4 carbon atoms, a chlorine or bromine atom, or a phenyl group.

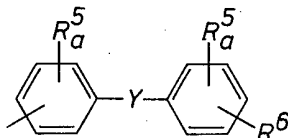
15 17. A method according to Claim 12, in which the photopolymerisable compound contains at least two groups of the formula 15



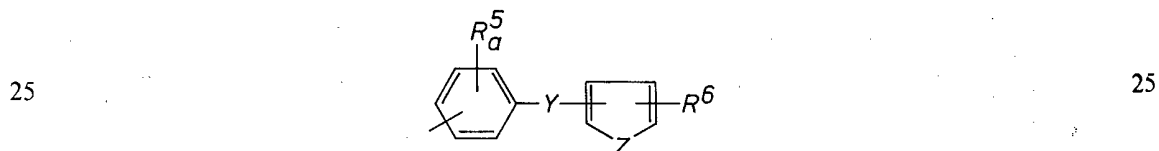
where

20 R^4 is an aliphatic or cycloaliphatic radical of 1 to 8 carbon atoms and 20
 a is zero or an integer of 1 to 4.

18. A method according to Claim 12, in which the photopolymerisable compound contains at least two groups of the formula



or



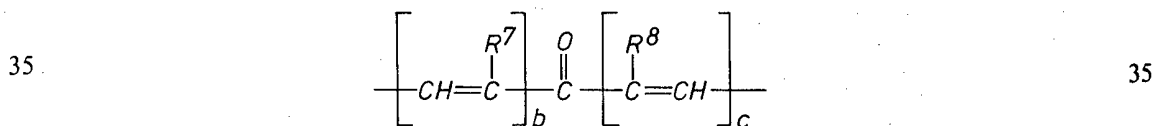
where

30 each R^5 is a halogen atom, or an alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkoxy, 30
cycloalkoxy, alkenoxy, cycloalkenoxy, carbalkoxy, carbocycloalkoxy,
carbalkenoxy, or carbocycloalkenoxy group, such organic groups containing 1 to 9
carbon atoms, or is a nitro group, or a carboxyl, sulphonic, or phosphoric acid
group in the form of a salt,

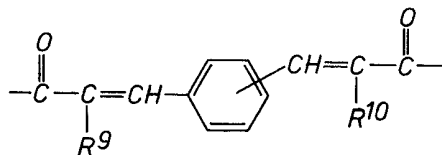
a has the meaning assigned in Claim 17,

R^b represents a valency bond or a hydrogen atom,

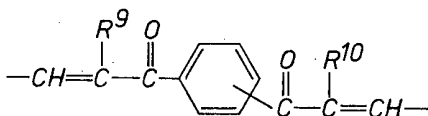
Y represents a grouping of formula



or



or



5 R^7 and R^8 are each individually a hydrogen atom, an alkyl group of 1 to 4 carbon atoms, or an aryl group, or R^7 and R^8 conjointly denote a polymethylene chain of 2 to 4 methylene groups, 5

R^9 and R^{10} are each a hydrogen atom, an alkyl group, or an aryl group, b and c are each zero, 1 or 2, with the proviso that they are not both zero, and Z is an oxygen or sulphur atom.

10 19. A method according to Claim 12, in which the photopolymerisable compound contains at least two groups of the formula 10



where

15 R^{11} is an aliphatic or mononuclear aromatic, araliphatic, or heterocyclyl group which has ethylenic unsaturation or aromaticity in conjugation with the ethylenic double bond shown, and 15

R has the meaning assigned in Claim 9.

20 20. A method according to any of Claims 7 to 10, wherein the photopolymerisable compound is irradiated in the presence of a photopolymerisation catalyst which, on irradiation, gives an excited state that leads to the formation of free radicals which then initiate polymerisation of the photopolymerisable compound. 20

25 21. A method according to Claim 20, in which the photopolymerisation catalyst is an organic peroxide or hydroperoxide, an α -halogen, substituted acetophenone, benzoin or an alkyl ether thereof, α -methylbenzoin, a benzophenone, a benzil acetal, an O -alkoxycarbonyl derivative of an oxime of either benzil or 1-phenylpropane - 1,2 - dione, an anthraquinone, or a photoredox system comprising an electron donor with either a phenothiazine dye or a quinoxaline. 25

30 22. A method according to any of Claims 11 to 19, wherein the photopolymerisable compound is irradiated in the presence of a photopolymerisation catalyst which, on irradiation, gives an excited state which transfers its energy to a molecule of the monomer giving rise to an excited molecule of the monomer which then crosslinks with an unexcited molecule of the monomer. 30

35 23. A method according to Claim 22, in which the photopolymerisation catalyst is 5-nitroacenaphthene, 4-nitroaniline, 2,4,7-trinitro-9-fluorenone, 3-methyl-1,3-diaza-1,9-benzanthrone, or a bis(dialkylamino)-benzophenone. 35

40 24. A method according to any of Claims 20 to 23, in which there is used from 0.1 to 20% by weight of the photopolymerisation catalyst, based on the weight of the photopolymerisable compound. 40

45 25. A method according to Claim 24, in which there is used from 0.5 to 15% by weight of the photopolymerisation catalyst, based on the weight of the photopolymerisable compound. 45

26. A method according to any preceding claim, in which actinic radiation of wavelength 200—600 nm is used. 45

27. A method according to any of Claims 2 to 26, in which the heat-curing agent is paraform or hexamethylenetetramine.

28. A method according to Claim 1, substantially as described herein.

50 29. A method according to Claim 1, substantially as described in any of Examples 1 to 6. 50

-
30. A method according to Claim 1, substantially as described in Example 7.
31. Articles having surfaces bonded by a method as claimed in any of Claims 1 to 27 and 29.
32. Articles having surfaces bonded by a method as claimed in Claim 28 or 30.

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