COMMONWEALTH of AUSTRALIA
PATENTS ACT 1952
APPLICATION FOR A STANDARD PATENT

We, M. R. GRACE & CO., of
1114 Avenue of the Americas,
New York, New York 10036,
United States of America.

86520/82

hereby apply for the grant of a Standard Patent for an invention entitled:

"THERMOSETTING ADHESIVE COMPOSITIONS"

which is described in the accompanying provisional specification.

Details of basic application(s):

<table>
<thead>
<tr>
<th>Number</th>
<th>Convention Country</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>317,646</td>
<td>United States of America</td>
<td>2 November, 1981</td>
</tr>
</tbody>
</table>

The address for service is care of DAVIES & COLLISON, Patent Attorneys, of 1 Little Collins Street, Melbourne, in the State of Victoria, Commonwealth of Australia.

Dated this 28 day of July 1982

To: THE COMMISSIONER OF PATENTS

(a member of the firm of DAVIES & COLLISON for and on behalf of the Applicant).
COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952
DECLARATION IN SUPPORT OF CONVENTION OR
NON-CONVENTION APPLICATION FOR A PATENT
86520/82

In support of the Application made for a patent for an invention
entitled: "THERMOSETTING ADHESIVE COMPOSITIONS"

1. WILLIAM WOODS McDOWELL, Jr.,
   of W.R. GRACE & CO.,
   of 1114 Avenue of the Americas,
   New York, New York 10036,
   United States of America

I do solemnly and sincerely declare as follows:—

1. (a) I am the applicant for the patent

(b) I am authorized by

W.R. GRACE & CO.

the applicant for the patent to make this declaration on its behalf.

2. (a) I am the actual inventor of the invention

(b) SHIOW CHING LIN of 6424 Elffolk Terr.
   Columbia, Maryland 21045, United States of America

is the actual inventor of the invention and the facts upon which the applicant is entitled to make the application are as follows:

the applicant is the assignee of the said actual inventor

3. The basic application as defined by Section 141 of the Act was made in the United States of America on the 2nd November, 1981 by Shiew Ching Lin in the name of the

4. The basic application referred to in paragraph 3 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

Declared at Columbia, this 15th day of July, 1982

William Woods McDowell, Jr.
Assistant Secretary

DAVIES & COLLISON, MELBOURNE and CANBERRA.

low molecular weight, low density polyethylene, are widely used in industry. These are for making corrugated cartons.
Polyurethane Adhesives

Claim

1. A thermoplastic, ethylenically unsaturated linear or cyclic reaction product of a substituted or unsubstituted acrylate ester of an epoxy resin containing at least one hydroxyl group and a polyisocyanate.

4. A process for adhering two substrates which comprises coating at least one of said substrates with a composition comprising

(a) a free radical thermal initiator and

(b) a thermoplastic, ethylenically unsaturated linear or cyclic reaction product of a substituted or unsubstituted acrylate ester of an epoxy resin containing at least one hydroxyl group and a polyisocyanate,

contacting the thus coated substrates and heating the thus contacted substrates in the range 100 - 300°C to cause adhesion.

The azo compound is added to the composition in an
COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(Original)

FOR OFFICE USE

8 6 5 2 0 / 8 2

Class Int. Class

Application Number: 8 6 5 2 0 / 8 2
Lodged:

Complete Specification Lodged: Accepted:
Published:

Priority:

Related Art:

Name of Applicant: W. R. GRACE & CO.

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Actual Inventor(s): SHIOW CHING LIN

Address for Service: DAVIES & COLLISON, Patent Attorneys,
1 Little Collins Street, Melbourne, 3000.

Complete specification for the invention entitled:
"THERMOSETTING ADHESIVE COMPOSITIONS"

The following statement is a full description of this invention,
including the best method of performing it known to us:

- 1 -
BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a novel compound which in combination with a free radical thermal initiator can be used as a hot melt adhesive or sealant composition which, on application of heat, preferably in an accelerated manner, crosslinks to give a thermoset bond or seal.

2. Description of the Prior Art

Conventional hot melt adhesive compositions are thermoplastic bonding materials which are solid at room temperature but become soft and fluid with good wettability of the adherent at elevated temperatures. These adhesives are readily applied in the molten state between adherends resulting in a strong adhesive thermoplastic bond on cooling and hardening.

Thermoplastic adhesives, which are used in the form of solutions, dispersions or solids, usually bond by purely physical means. Probably the most important means of applying thermoplastic adhesives is the hot melt method wherein bond formation occurs when the polymer melt solidifies in position between adherends. The bonds obtained by this method reach their final strength faster than those obtained from solution type adhesives. Obviously, the thermal stability of the thermoplastic resin determines its potential usefulness as a hot melt adhesive. In order for the thermoplastic to be used as a hot melt, it must also have a low melt viscosity, thus permitting application of the adhesive to the adherends at acceptable rates. Usually this means the polymer must have a low molecular weight. However, many thermoplastic materials cannot be employed as hot melts because they do not have sufficient cohesive strength at the low molecular weights required for application to a substrate. For example, the low molecular weight polyolefins, especially...
low molecular weight, low density polyethylene, are widely used in hot melt adhesives for sealing corrugated cartons, multi-wall bag seaming and the like, but they do not have sufficient strength to be used in structural applications such as plywood manufacture. Further, they do not have sufficient heat resistance to be used for bonding components which are intermittently exposed to elevated temperatures such as under the hood automotive applications. That is, thermoplastic adhesives cannot be employed where the adhesive in situ is reexposed to elevated temperatures which will cause the adhesive to sag thereby allowing the bond to break.

The concept of thermosetting or crosslinking resin adhesive is also known in the art. Many resin adhesives which undergo an irreversible, chemical and physical change and become substantially insoluble are known. Thermosetting adhesives comprising both condensation polymers and addition polymers are also known and examples include the urea-formaldehyde, phenol-formaldehyde and melamine-formaldehyde adhesives; epoxy, unsaturated polyester and polyurethane adhesives. More particularly, U. S. 3,723,568 teaches the use of polyepoxides and optional epoxy polymerization catalysts. U. S. 4,122,073 teaches thermosetting resin obtained from polyisocyanates, polyanhydrides and polyepoxides. Crosslinking in these patents is achieved by reaction with available sites in the base polymers. U. S. 4,137,364 teaches crosslinking of an ethylene/vinyl acetate/vinyl alcohol terpolymer using isophthaloyl, bis-caprolactam or vinyl triethoxy silane whereby crosslinking is achieved before heat activation with additional crosslinking induced by heat after application of the adhesive. U. S. 4,116,937 teaches a further method of thermal crosslinking by the use of polyamino bis-maleimide class of flexible
polyimides, which compounds can be hot melt extruded up to 150°C and undergo crosslinking at elevated temperatures thereafter. In these latter two patents, thermal crosslinking is also achieved by reactions of the particular crosslinking agent with available sites of the base polymers. U. S. 3,934,056 teaches resin compositions of high adhesivity comprising ethylene-vinyl acetate copolymer, chlorinated or chlorosulfonated polyethylene, unsaturated carboxylic acids and an organic peroxide.

Another thermosetting adhesive is known from U. S. 3,945,877 wherein the composition comprises a coal tar pitch, ethylene/vinyl acetate copolymer and ethylene/acrylic acid copolymer plus a crosslinking agent such as dicumyl peroxide.

In many of these prior art thermosetting adhesive compositions admixture of 2, 3 or 4 components is necessary in order to get a thermoset bond. Thus, the resultant bond depends on the homogeneity of the admixture. Further, in many cases, e. g., epoxy adhesives, two or more components must be admixed just prior to the preparation of the bond. This necessitates a fast application since the crosslinking reaction begins immediately upon admixture and is irreversible.

OBJECTS OF THE INVENTION

One object of the instant invention is to produce an adhesive composition which is solventless. Another object of the invention is to produce an adhesive composition which can be applied as a hot melt. Still another object of the instant invention is to produce an adhesive composition which is heat curable in a minimum time period. A further object of the invention is to produce a novel compound which in combination with a free radical thermal initiator will result in a thermoset coating, adhesive or sealant on heating. Yet another object of the
invention is to produce an adhesive composition which can be applied as a hot melt and thereafter cured by a thermally triggered initiator to a thermoset adhesive at a more elevated temperature. Other objects will become apparent from a reading hereinafter.

DESCRIPTION OF THE INVENTION

The present invention relates to an ethylenically unsaturated linear or cyclic thermoplastic reaction product of an acrylate or methacrylate ester of an epoxy resin containing at least 1 and preferably two hydroxyl groups and a polyisocyanate, preferably a diisocyanate.

The compound in combination with a free radical thermal initiator, upon heating and applied to the parts to be bonded or sealed, can be heated to a more elevated temperature to trigger the free radical thermal initiator to form a thermoset bond or seal.

Some of the acrylate or methacrylate ester of an epoxy resin containing at least one hydroxyl group used herein are commercially available materials. One of such materials is Shell Co.’s Epocryl Resin-370 having the idealized structure:

\[
\begin{align*}
O & \quad OH \\
\text{CH}_2=\text{CH-C-O-CH}_2-\text{CH-CH}_2-O & \quad \left[ \begin{array}{c}
\text{CH}_2=\text{CH-CH}_2-O-\text{CH}_2-\text{CH-CH}_2-O \\
\text{O-CH}_2-\text{CH-CH}_2-O-C=\text{CH}_2
\end{array} \right] \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

This material has a viscosity of 9,000 poises at 25°C and contains 0.02 equivalents epoxide/100 g. The material is formed from the reaction of one mole of diglycidyl ether of bisphenol A reacted with two moles of acrylic acid.
Aside from substituted and unsubstituted acrylic acid being used to form the compound herein, hydroxylalkyl acrylate half esters of oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelic, sebacic, phthalic, terephthalic, isophthalic acid and mixtures thereof are also operable. Thus, a generalized reaction for forming substituted or unsubstituted acrylate esters of an epoxy resin is as follows:

\[
\begin{align*}
CH=C-\begin{array}{c}
\text{O} \\
\text{COCH_2CHOC-P_4}
\end{array} & \text{O} \text{COH} + R_1(CH_2)_n \rightarrow \text{O} \\
R_2 & \begin{array}{c}m \\
\text{R}_3
\end{array}
\end{align*}
\]

wherein \( m \) is 0 or 1; \( n \) is 1 to 4; \( R_2 \) and \( R_3 \) are H or \( CH_3 \); \( R_4 \) is \(-CH=CH-, -C=CH_2-, \) or \(-CH_2-p; \)

\( p \) is 0 to 6 and \( R_1 \) is an organic moiety with the valence of \( n \).

The substituted or unsubstituted acrylate ester of the epoxy resin (I) is then reacted through its hydroxyl groups with a polyisocyanate to form the compound of the instant invention, to wit:

\[
I + R_5-(NCO)_q \rightarrow
\]
wherein $R_5$ is an organic moiety with the valence of $q$ and $q$ is 2 to 4 and the remaining symbols are as shown above.

The resulting thermoplastic, urethane-containing, ethylenically unsaturated material (II) can then be admixed with a free radical thermal initiator, e.g., an organic peroxide and cured through the unsaturated groups to a thermoset adhesive, sealant or coating.

The epoxy resin to be used in the composition of the invention comprises those materials possessing at least one, e.g., glycidol, and preferably more than one epoxy group, i.e.,

$$\begin{align*}
\text{O} & \\
\text{C-C} & \\
\end{align*}$$

These compounds may be saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic and may be substituted with substituents, such as chlorine hydroxyl groups, ether radicals and the like. They may be monomeric or polymeric.

For clarity, many of the polyepoxides and particularly those of the polymeric type are described in terms of epoxy equivalent values. The meaning of this expression is described in U.S. 2,633,458. The polyepoxides used in the present composition and process are those having an epoxy equivalency greater than 1.0.
Various examples of polyepoxides that may be used in the composition and process of this invention are given in U. S. 2,633,458 and it is to be understood that so much of the disclosure of that patent relative to examples of polyepoxides is incorporated by reference into this specification.

Other examples include the epoxidized esters of the polyethylenically unsaturated monocarboxylic acids, such as epoxidized linseed, soybean, perilla, oiticica, tung, walnut and dehydrated castor oil, methyl linoleate, butyl linoleate, ethyl 9,12-octadecadienoate, butyl 9,12,15-octadecatrienoate, butyl eleostearate, monoglycerides of tung oil fatty acids, monoglycerides of soybean oil, sunflower, rapeseed, hempseed, sardine, cottonseed oil and the like.

Another group of the epoxy-containing materials used in the composition and process of this invention include the epoxidized esters of unsaturated monohydric alcohols and polycarboxylic acids. For example, di(2,3-epoxybutyl) adipate, di(2,3-epoxybutyl) oxalate, di(2,3-epoxyhexyl succinate, di(3,4-epoxybutyl) maleate, di(2,3-epoxyoctyl) pimelate, di(2,3-epoxybutyl) phthalate, di(2,3-epoxyoctyl) tetrahydrophthalate, di(4,5-epoxy-dodecyl) maleate, di(2,3-epoxybutyl) tetraphthalate, di(2,3-epoxypentyl) thiouropionate, di(5,6-epoxy-tetradecyl) diphenyl-dicarboxylate, di(3,4-epoxyheptyl) sulfonyledibutyrate, tri(2,3-epoxybutyl) 1,2,4-butane-tricarboxylate, di(5,6-epoxypentadecyl) tartarate, di(4,5-epoxytetradecyl) maleate, di(2,3-epoxybutyl)-azelate, di(3,4-epoxybutyl) citrate, di(5,6-epoxyoctyl cyclohexane-1,2-dicarboxylate, di(4,5-epoxyoctadecyl) maleate.

Still another group comprises the epoxidized polyethylenically unsaturated hydrocarbons, such as epoxidized 2,2-bis(2-cyclohexenyl) propane, epoxidized vinyl cyclohexene and epoxidized dimer of cyclopentadiene.
Another group comprises the epoxidized polymers and copolymers of diolefins, such as butadiene. Examples of this include, among others, butadiene-acrylonitrile copolymers (Bycar rubbers), butadiene-styrene copolymers and the like.

Another group comprises the glycidyl containing nitrogen compounds, such as diglycidyl aniline and di- and triglycidylamine.

The polyepoxides that are particularly preferred for use in the compositions of the invention are the glycidyl ethers and particularly the glycidyl ethers of polyhydric phenols and polyhydric alcohols. The glycidyl ethers of polyhydric phenols are obtained by reacting epichlorohydrin with the desired polyhydric phenols in the presence of alkali. Polyether-A and Polyether-B described in the above-noted U.S. 2,633,458 are good examples of polyepoxides of this type. Other examples include the polyglycidyl ether of 1,1,2,2-tetrakis(4-hydroxyphenyl)-ethane (epoxy value of 0.45 eq./100 g) and melting point 85°C, polyglycidyl ether of 1,1,5,5-tetraakis(hydroxyphenyl)pentane (epoxy value of 0.514 eq./100 g) and the like and mixtures thereof.

Additional examples of epoxy resins operable herein include, but are not limited to, diglycidyl isophthalate, diglycidyl phthalate, a-glycidyl phenyl glycidyl ether, diglycidyl ether of resorcinol, triglycidyl ether of phloroglucinol, triglycidyl ether of methyl phloroglucinol, 2,6-(2,3-epoxypropyl)phenylglycidyl ether, [4-(2,3-epoxy)propoxy-N,N-bis(2,3-epoxypropyl)aniline, 2,2-bis[p-2,3-epoxypropoxy]phenyl] propane, diglycidyl ether of bisphenol-A, diglycidyl ether of bisphenol-hexafluoroacetone, diglycidyl ether of 2,2-bis(4-hydroxyphenyl)nonadecane, diglycidyl phenyl ether, triglycidyl 4,4-bis(4-hydroxyphenyl)pentanoic acid,
diglycidyl ether of tetrachlorobisphenol-A, diglycidyl ether of tetrabromobisphenol-A, triglycidyl ether of trihydroxybiphenyl, tetraglycidoxy biphenyl, [tetrakis(2,3-epoxypropoxy)diphenylmethane], [2,2',4,4'-tetraakis(2,3-epoxypropoxy)benzophenone, 3,9-bis[2-(2,3-epoxypropoxy)-phenylethyl]-2,4,8,10-tetraoxaspiro[5,5]undecane, triglycidoxy-1,1,3-triphenylpropane, tetraglycidoxy tetraphenylethane, polyglycidyl ether of phenol-formaldehyde novolac, polyglycidyl ether of o-cresol-formaldehyde novolac, diglycidyl ether of butanediol, di(2-methyl)glycidyl ether of ethylene glycol, polychlorohydrin di(2,3-epoxy-propyl)ether, diglycidyl ether of polypropylene glycol, epoxidized polybutadiene, epoxidized soybean oil, triglycidyl ether of glycerol, triglycidyl ether of trimethylol-propane, polyallyl glycidyl ether, 2,4,6,8,10-pentakis-[3-(2,3-epoxypropoxy)-propyl]2,4,6,8,10-pentamethylcyclopentasiloxane, diglycidyl ether of chloroendic diol, diglycidyl ether of dioxanediol, diglycidyl ether of endomethylene cyclohexanediol, diglycidyl ether of hydrogenated bisphenol-A, vinylcyclohexene d'oxide, limonene dioxide, dicyclopentadiene dioxide, p-epoxycyclopentenylphenyl glycidyl ether, epoxycyclopentenylphenyl glycidyl ether, o-epoxycyclopentenylphenyl glycidyl ether, bis-epoxycyclopentenyl ether of ethylene glycol, (2-3,4-epoxy)-cyclohexyl-5,5-spiro(3,4-epoxy)-cyclohexane-m-dioxane, 1,3-bis[3-(2,3-epoxypropoxy)propyl]tetramethyldisiloxane, epoxidized polybutadiene, triglycidyl ester of linoleic trimer acid, epoxidized soybean oil, diglycidyl ester of linoleic dimer acid, 2,2-bis[4-(2,3-epoxypropyl)cyclohexyl]propane, 2,2-[4-[3-chloro-2-(2,3-epoxypropoxy)-propolyl]cyclohexyl]propane, 2,2-bis[3,4-epoxycyclohexyl]propane, bis(2,3-epoxycyclopentyl)ether (liquid isomer), bis(2,3-epoxycyclopentyl)ether (solid isomer),
1,2-epoxy-6-(2,3-epoxypropoxy)hexahydro-4,7-methanoindane, 3,4-epoxycyclohexylmethyl-(3,4-epoxy)cyclohexane carboxylate, 3,4-epoxy-6-methylcyclohexylmethyl-4-epoxy-6-methylcyclohexane carboxylate and bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate. Tri and tetrafunctional epoxides such as triglycidyl isocyanurate and tetraphenylethylene epoxy are also operable herein.

The polyisocyanates employed in the instant invention to form the adhesive composition can be aromatic, aliphatic, cycloaliphatic and combinations thereof. Preferred are the diisocyanates, but tri and tetraisocyanates are also operable. More specifically, illustrative of the diisocyanates are 2,4-toluene diisocyanate, m-phenylene diisocyanate, xylylene diisocyanate, 4-chloro-1,3-phenylene diisocyanate, 4,4'-biphenylene diisocyanate, 1,4-tetramethylene and 1,6-hexamethylene diisocyanate, 1,4-cyclohexylene diisocyanate, 1,5-tetrahydronaphthalene diisocyanate and methylene dicyclohexylene diisocyanate. Diisocyanates in which each of the diisocyanate groups is directly attached to a ring are preferred since usually they react more rapidly.

Other diisocyanates which may be used are the high molecular weight diisocyanates obtained by reacting polyamines containing terminal primary or secondary amine groups or dihydric alcohols. For example: 2 moles of diisocyanate R₅(NCO)₂ are reacted with 1 mole of a diol OH-R₆-OH to form a chain extended diisocyanate, i.e.,

\[
\begin{align*}
O & \quad O \\
OCN-R₅-NHCO-R₆-OCHN-R₅-NCO \\
\end{align*}
\]
wherein $R_5$ and $R_6$ are divalent organic moieties. Thus, the alkane and alkene polyols such as 1,5-pentene diol, ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, "Bisphenol-A" and substituted "Bisphenol-A" are operable herein to chain-extend the diisocyanate reactant. These diols can have molecular weights ranging from about 200 up to about 20,000, the high end of the molecular weight being used when the diisocyanate formed is reacted with a low molecular weight unsaturated monohydroxyl material.

Additionally, unsaturated diisocyanates can also be employed. These materials, for example, can be formed from diols such as the family of hydroxyl terminated homopolymers and copolymers, commercially available from ARCO under the tradename "Poly bd" resins. Such resins include butadiene homopolymers of the formula:

$$\text{HO-} \left[ \left( \text{CH}_2 \text{CH-CH-CH}_2 \right)_{x} \left( \text{CH}_2 \text{CH-CH}_2 \right)_{y} \right] \text{OH}$$

wherein $n$ is about 50, and styrene-butadiene and acrylonitrile-butadiene copolymer diols of the formula:

$$\text{HO-} \left[ \left( \text{CH}_2 \text{CH-CH-CH}_2 \right)_a \left( \text{CH-CH}_2 \right)_b \right] \text{OH}$$

wherein

- $X = 0$ for styrene-butadiene copolymer
- $X = \text{CN}$ for acrylonitrile-butadiene copolymer

- $a = 0.75$
- $b = 0.25$
- $n = 54$
- $a = 0.85$
- $b = 0.15$
- $n = 78-87$
One mole of these unsaturated polyols will react with two moles of a diisocyanate to form a chain-extended diisocyanate having unsaturation in the backbone thereof.

The thermal initiators used herein are free radical initiators selected from substituted or unsubstituted pinacols, azo compounds, thiurams, organic peroxides and mixtures thereof.

The organic peroxides operable are of the general formula:

\[ R-O-O-(R_1-O-O)_n-R \]

wherein \( n = 0 \) or \( 1 \), \( R \) is independently selected from hydrogen, aryl, alkyl, aryl carbonyl, alkaryl carbonyl, aralkyl carbonyl and alkyl carbonyl and \( R_1 \) is alkyl or aryl, said alkyl groups containing 1 to 20 carbon atoms.

Examples of operable organic peroxides include, but are not limited to, 2,5-dimethyl-2,5-di(t-butyperoxy)hexane, 1,3-bis(t-butyperoxyisopropyl)benzene, 1,3-bis-(cumylperoxyisopropyl)benzene, 2,4-dichlorobenzoyl peroxide, caprylyl peroxide, lauroyl peroxide, t-butyl peroxysobutyrate, benzoyl peroxide, p-chlorobenzoyl peroxide, hydroxyheptyl peroxide, di-t-butyl diperphthalate, t-butyl peracetate, t-butyl perbenzoate, dicumyl peroxide, 1,1-di(t-butyperoxy)-3,3,5-trimethylcyclohexane and di-t-butyl peroxide.

The organic peroxide is added to the composition in an amount ranging from 0.01 - 10%, preferably 0.1 - 5%, by weight based on the weight of the composition.

Examples of azo compounds operable herein include, but are not limited to, commercially available compounds such as 2-t-butylnazo-2-cyanopropane; 2,2'-azobis-(2,4-dimethyl-4-methoxy-valeronitrile); 2,2'-azobis-(isobutyronitrile); 2,2'-azobis(2,4-dimethylvaleronitrile) and 1,1'-azobis-(cyclohexane-carbonitrile).
The azo compound is added to the composition in an amount ranging from 0.001 - 5%, preferably 0.01 - 2% by weight based on the weight of the composition.

The thiurams operable as thermal initiators herein are of the formula

\[ \text{S} \begin{array}{c} \text{R}_1 \\ \text{R}_2 \end{array} \text{N-C-S-S-C-N} \begin{array}{c} \text{R}_3 \\ \text{R}_4 \end{array} \]

wherein \( \text{R}_1, \text{R}_2, \text{R}_3 \) and \( \text{R}_4 \) taken singly can be hydrogen, linear or branched alkyl having from 1 to about 12 carbon atoms, linear or branched alkenyl having from 2 to about 12 carbon atoms, cycloalkyl having from 3 to about 10 ring carbon atoms, cycloalkenyl having from 3 to about 10 ring carbon atoms, aryl having from 6 to about 12 ring carbon atoms, aralkyl having from 6 to about 12 ring carbon atoms, and, when taken together, \( \text{R}_1 \) and \( \text{R}_2 \) and \( \text{R}_3 \) and \( \text{R}_4 \) can each be a divalent alkylene group \((-\text{C}_{\text{n}}\text{H}_{2\text{n}}\) having from 2 to about 12 carbon atoms, a divalent alkenylene group \((-\text{C}_{\text{n}}\text{H}_{2\text{n}-1}\) having from 3 to about 10 carbon atoms, a divalent alkadienylene group \((-\text{CH}_{\text{n}}\) having from 5 to about 10 carbon atoms, a divalent alkatrienylene group \((-\text{C}_{\text{n}}\text{H}_{2\text{n}-3}\) having from 5 to about 10 carbon atoms, a divalent alkyleneoxyalkylene group \((-\text{C}_{\text{x}}\text{H}_{2\text{x}}\text{OC}_{\text{x}}\text{H}_{2\text{x}}\) having a total of from 4 to about 12 carbon atoms, or a divalent alkyleneaminoalkylene group \((-\text{C}_{\text{x}}\text{H}_{2\text{x}}\text{NC}_{\text{x}}\text{H}_{2\text{x}}\) having a total of from 4 to about 12 carbon atoms.

Example 5
Operable thiurams include, but are not limited to, tetramethylthiuram disulfide, tetraethylthiuram disulfide, di-N-pentamethylenethiuram disulfide, tetrabutylthiuram disulfide, diphenyl(dimethylthiuram disulfide, diphenyl-diethylthiuram disulfide and diethylenedioxythiuram disulfide and the like.

The thiuram is added to the composition in an amount ranging from 0.005-5.0% by weight of the composition.

The substituted or unsubstituted pinacols operable herein as a thermal initiator have the general formula:

\[
\begin{array}{c}
\text{R}_1 \quad \text{R}_3 \\
\text{R}_2 - \text{C} - \text{C} - \text{R}_4 \\
\text{X} \quad \text{Y}
\end{array}
\]

wherein \(R_1\) and \(R_3\) are the same or different substituted or unsubstituted aromatic radicals, \(R_2\) and \(R_4\) are substituted or unsubstituted aliphatic or aromatic radicals and \(X\) and \(Y\) which may be the same or different are hydroxyl, alkoxy or aryloxy.

Preferred pinacols are those wherein \(R_1\), \(R_2\), \(R_3\) and \(R_4\) are aromatic radicals, especially phenyl radical and \(X\) and \(Y\) are hydroxyl.

Examples of this class of compounds include, but are not limited to, benzopinacol, 4,4'-dichlorobenzopinacol, 4,4'-dibromobenzopinacol, 4,4'-diiodobenzopinacol, 4,4',4'',4'''-tetrachlorobenzopinacol, 2,4-2',4'-tetrachlorobenzopinacol, 4,4'-dimethylbenzopinacol, 3,3'-dimethylbenzopinacol, 2,2'-dimethylbenzopinacol, 3,4,3',4'-tetramethylbenzopinacol, 4,4'-dimethoxybenzopinacol, 4,4',4',4''-tetramethoxybenzopinacol, 4,4',4',4''-tetrachlorobenzopinacol, 4,4'-diphenylbenzopinacol, 4,4' dichloro-4',4''-dinitremethylbenzopinacol, 4,4'-dimethyl-4',4''-diphenylbenzopinacol, xanthopinacol, fluorenepinacol, acetophenonepinacol, 4,4' dimethylacetophenone-pinacol, 4,4'-dichloracetophenonepinacol,
example, the low molecular weight polyolmers, especially

1,1,2-triphenyl-propane-1,2-diol, 1,2,3,4-tetraphenyl-
butane-2,3-diol, 1,2-diphenylcyclobutane-1,2-diol,
propiophenone-pinacol, 4,4'-dimethylpropiophenone-
pinacol, 2,2'-ethyl-3,3'-dimethoxypropiophenone-pinacol,
1,1,1,4,4,4-hexafluoro-2,3-diphenyl-butane-2,3-diol.

As further compounds according to the present
invention, there may be mentioned: benzopinacol-mono
methylether, benzopinacol-mono-phenylether, benzopinacol
and monoisopropyl ether, benzopinacol monoisobutyl ether,
benzopinacol mono (diethoxy methyl) ether and the like.

The pinacol is added to the composition in amounts
ranging from 0.01 - 10%, preferably 0.1 - 5%, by weight
based on the weight of the composition.

The heating step is usually carried out for a period
of 10 seconds to 30 minutes at a temperature of 100 -
300°C, preferably 120 - 200°C which is sufficient to fully
cure the composition to a solid adhesive or sealant
product.

The heating step using a thermal initiator to cure the
adhesive organic resin composition can be accomplished in
several ways. In simple systems, the adhesive composition
can be applied by manual means to an adherend, contacted
with another adherend and the assembled system heated in a
forced air oven until a thermostet bond results.

Additionally and preferably, electromagnetic heating
can be utilized as a faster and more efficient means of
curing, especially where the substrates to be bonded are
plastic materials. In addition to the formation of high
strength bonds, electromagnetic bonding techniques aid in
(a) fast bond setting times, and (b) automated part
handling and assembly.

In practicing the instant invention, electromagnetic
heating can be employed with the adhesive composition
herein to adhere (l) plastic to plastic, (2) plastic to
3. A process for adhering two substrates which

metal and (3) metal to metal. For example, dielectric heating can be used to bond (1) and (2) supra if the adhesive composition contains sufficient polar groups to heat the composition rapidly and allow it to bond the adherends. Inductive heating can also be used to bond (1), (2) and (3). That is, when at least one of the adherends is an electrically conductive or ferromagnetic metal, the heat generated therein is conveyed by conductance to the adhesive composition thereby initiating the cure to form a thermoset adhesive. In the instance where both adherends are plastic, it is necessary to add an energy absorbing material, i.e., an electrically conductive or ferromagnetic material, preferably in fiber or particle form (10-400 mesh) to the adhesive composition. The energy absorbing material is usually added in amounts ranging from 0.1 to 2 parts by weight, per 1 part by weight of the adhesive organic resin composition. It is also possible to impregnate the plastic adherend at the bonding joint with particles of the energy absorbing material in order to use inductive heating, but care must be exercised that the plastic is not distorted.

The particulate electromagnetic energy absorbing material used in the adhesive composition when induction heating is employed can be one of the magnetizable metals including iron, cobalt and nickel or magnetizable alloys or oxides of nickel and iron and nickel and chromium and iron oxide. These metals and alloys have high Curie points (730°-2,040°F).

Electrically conductive materials operable herein when inductive heating is employed include, but are not limited to, the noble metals, copper, aluminum, nickel, zinc as well as carbon black, graphite and inorganic oxides.
There are two forms of high frequency heating operable herein, the choice of which is determined by the material to be adhered. The major distinction is whether or not the material is a conductor or non-conductor of electrical current. If the material is a conductor, such as iron or steel, then the inductive method is used. If the material is an insulator, such as wood, paper, textiles, synthetic resins, rubber, etc., then dielectric heating can also be employed.

Most naturally occurring and synthetic polymers are non-conductors and, therefore, are suitable for dielectric heating. These polymers may contain a variety of dipoles and ions which orient in an electric field and rotate to maintain their alignment with the field when the field oscillates. The polar groups may be incorporated into the polymer backbone or can be pendant side groups, additives, extenders, pigments, etc. For example, as additives, lossy fillers such as carbon black at a one percent level can be used to increase the dielectric response of the adhesive. When the polarity of the electric field is reversed millions of times per second, the resulting high frequency of the polar units generates heat within the material.

The uniqueness of dielectric heating is in its uniformity, rapidity, specificity and efficiency. Most plastic heating processes such as conductive, convective or infrared heating are surface-heating processes which need to establish a temperature within the plastic and subsequently transfer the heat to the bulk of the plastic by conduction. Hence, heating of plastics by these methods is a relatively slow process with a non-uniform temperature resulting in overheating of the surfaces. By contrast, dielectric heating generates the heat within the material and is therefore uniform and rapid, eliminating
the need for conductive heat transfer. In the dielectric heating system herein the electrical frequency of the electromagnetic field is in the range 1-3,000 megahertz, said field being generated from a power source of 0.5-1,000 kilowatts.

Induction heating is similar, but not identical, to dielectric heating. The following differences exist: (a) magnetic properties are substituted for dielectric properties; (b) a coil is employed to couple the load rather than electrodes or plates; and (c) induction heaters couple maximum current to the load. The generation of heat by induction operates through the rising and falling of a magnetic field around a conductor with each reversal of an alternating current source. The practical deployment of such field is generally accomplished by proper placement of a conductive coil. When another electrically conductive material is exposed to the field, induced current can be created. These induced currents can be in the form of random or "eddy" currents which result in the generation of heat. Materials which are both magnetizable and conductive generate heat more readily than materials which are only conductive. The heat generated as a result of the magnetic component is the result of hysteresis or work done in rotating magnetizable molecules and as a result of eddy current flow. Polyolefins and other plastics are neither magnetic nor conductive in their natural states. Therefore, they do not, in themselves, create heat as a result of induction.

The use of the electromagnetic induction heating method for adhesive bonding of plastic structures has proved feasible by interposing selected electromagnetic energy absorbing materials in an independent adhesive composition layer or gasket conforming to the surfaces to be bonded,
electromagnetic energy passing through the adjacent plastic structures (free of such energy absorbing materials) is readily concentrated and absorbed in the adhesive composition by such energy absorbing materials thereby rapidly initiating cure of the adhesive composition to a thermoset adhesive.

Electromagnetic energy absorbing materials of various types have been used in the electromagnetic induction heating technique for some time. For instance, inorganic oxides and powdered metals have been incorporated in bond layers and subjected to electromagnetic radiation. In each instance, the type of energy source influences the selection of energy absorbing material. Where the energy absorbing material is comprised of finely divided particles having ferromagnetic properties and such particles are effectively insulated from each other by particle containing nonconducting matrix material, the heating effect is substantially confined to that resulting from the effects of hysteresis. Consequently, heating is limited to the "Curie" temperature of the ferromagnetic material or the temperature at which the magnetic properties of such material cease to exist.

The electromagnetic adhesive composition of this invention may take the form of an extruded ribbon or tape, a molded gasket or cast sheet. In liquid form it may be applied by brush to surfaces to be bonded or may be sprayed on or used as a dip coating for such surfaces.

The foregoing adhesive composition, when properly utilized as described hereinafter, results in a solvent free bonding system which permits the joining of metal or plastic items without costly surface pretreatment. The electromagnetically induced bonding reaction occurs rapidly and is adaptable to automated fabrication techniques and equipment.
To accomplish the establishment of a concentrated and specifically located heat zone by induction heating in the context of bonding in accordance with the invention, it has been found that the electromagnetic adhesive compositions described above can be activated and a bond created by an induction heating system operating with an electrical frequency of the electromagnetic field of from about 5 to about 30 megacycles and preferably from about 15 to 30 megacycles, said field being generated from a power source of from about 1 to about 30 kilowatts, and preferably from about 2 to about 5 kilowatts. The electromagnetic field is applied to the articles to be bonded for a period of time of less than about 2 minutes.

As heretofore mentioned, the electromagnetic induction bonding system and improved electromagnetic adhesive compositions of the present invention are applicable to the bonding of metals, thermoplastic and thermoset material, including fiber reinforced thermoset material.

It is critical in practicing the instant invention that the ethylenically unsaturated reaction product of the composition be linear or cyclic, i.e., a thermoplastic, prior to its use with a free radical thermal initiator. Thus, the number of OH groups present in the substituted or unsubstituted acrylate ester of the epoxy resin prior to reaction with the polyisocyanate can be any number, preferably 2, depending on the functionality of the polyisocyanate reacted therewith and the equivalent ratio of -OH to -NCO in the reaction. For example, a monoepoxide, i.e., glycidol, can be reacted with a substituted or unsubstituted acrylic acid:
wherein R is an alkyl group or hydrogen.

This material containing two OH groups is then reacted with a diisocyanate OCN-R-NCO to form a polyurethane:

$$\text{III} + \text{OCN-R-NCO} \rightarrow \text{IV}$$

where $n$ can be any number depending on the mole ratio of III and isocyanate.

The resulting thermoplastic, urethane-containing, ethylenically unsaturated material can then be admixed with a free radical thermal initiator, e.g., a peroxide, and cured through the unsaturated groups to a thermoset adhesive by heating.
Additionally, a diepoxide can be used, e.g.,

\[
\begin{align*}
\text{CH}_2=\text{CH-R'} & \quad \text{CH} \quad \text{CH}_2 + 2 \text{CH}_2=\text{C}=\text{COOH} \\
\downarrow & \\
\text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH}
\end{align*}
\]

Again this is reacted stoichiometrically with a diisocyanate to form a polyurethane:

\[
\begin{align*}
\text{V} & + \text{OCN-R-NCO} \\
\downarrow & \\
\sim(\text{O-CH-R'-CH-OC-NH-R-NH-C})_n \quad \text{CH}_2 \quad \text{CH}_2 \\
\end{align*}
\]

wherein \( n \) depends on the mole ratio of \( V \) and isocyanate.

The resulting thermoplastic material will form a thermoset material useful as an adhesive, sealant or coating on heating with a free radical thermal initiator.

An ethylenically unsaturated polymeric type material containing more than 2 OH groups such as epocryl resin, commercially available from Shell Chemical Co., i.e.,

\[
\begin{align*}
\text{CH}_2=\text{CR-C-O-CH}_2 \quad \text{CH-CH}_2-O[ & \quad \text{OH} \\
\text{OH} & \quad \text{OH} \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]
where R = any alkyl group or hydrogen and n is 0.2, can also be used when less than a stoichiometric amount of a diisocyanate is reacted therewith. That is, in systems containing bifunctional monomers a high degree of polymerization is attained only when the reaction is forced almost to completion. The introduction of a trifunctional monomer into the reaction produces a rather startling change which is best illustrated using a modified form of the Carothers equation. A more general functionality factor $f_{av}$ is introduced, defined as the average number of functional groups present per monomer unit. For a system containing $N_0$ molecules initially and equivalent numbers of two function groups A and B, the total number of functional groups is $N_0 f_{av}$. The number of groups that have reacted in time $t$ to produce $N$ molecules is then $2(N_0 - N)$ and

$$p = 2(N_0 - N)/N_0 f_{av}$$

The expression for $x_n$ then becomes

$$x_n = 2/(2 - pf_{av})$$

but this is only valid when equal numbers of both functional groups are present in the system.

For a completely bifunctional system such as an equimolar mixture of an acrylate or methacrylate ester of an epoxy resin containing two hydroxyl groups, i.e., an unsaturated diol and diisocyanate, $f_{av} = 2$, and $x_n = 20$ for $p = 0.95$. If, however, a trifunctional alcohol is added so that the mixture is composed of 2 mol diisocyanate, 1.4 mol diol, and 0.4 mol of triol, $f_{av}$ increases to

$$f_{av} = (2 \times 2 + 1.4 \times 2 + 0.4 \times 3)/3.8 = 2.1.$$  

The value of $x_n$ is now 200 after 95 per cent conversion, but only a small increase to 95.23 per cent is required for $x_n$ to approach infinity - a most dramatic increase.
This is a direct result of incorporating a trifunctional unit in a linear chain where the unreacted hydroxyl provides an additional site for chain propagation. This leads to the formation of a highly branched structure and the greater the number of multi-functional units the faster the growth into an insoluble three-dimensional network. When this happens, the system is said to have reached its gel point, i.e., the system is thermoset. In the instant invention it is critical that the composition remain thermoplastic and not reach its gel point prior to use as a coating, sealant or hot melt adhesive.

The reaction to form the hydroxyl-containing, substituted or unsubstituted acrylate esters of an epoxy resin reactant herein is carried out in the presence of a catalyst at temperatures ranging from 80-150°C, preferably 90-125°C. Known catalysts include, but are not limited to, triphenyl phosphine, triisopropylamine and 3-(p-Chlorophenyl)-1,1-dimethylurea. These catalysts are added to the reaction in amounts ranging from 0.1 - 1.2 parts per 100 parts of the epoxy resin.

The reaction between the hydroxyl-containing, substituted or unsubstituted acrylate esters of an epoxy resin and the polyisocyanate in the instant invention is preferably carried out in the presence of the free radical thermal initiator in order to uniformly disperse said initiator throughout the solid resulting reaction product. Thus, the reaction is carried out at a temperature below the decomposition temperature of the thermal initiator, e.g., at a temperature ranging from 20-80°C. The reaction is performed in the presence of a catalytic amount, i.e., 0.01-5% by weight of the reactants of well known urethane-forming catalysts. Such catalysts include, but are not limited to, triphenyl phosphine, dibutyl tin dilaurate, stannous octoate and the like.
In the instances, where the decomposition temperature of the free radical thermal initiator is below the reaction temperature of the urethane-forming reaction, the thermal initiator is added to the thermoplastic, ethylenically unsaturated, urethane-containing compound after it has been cooled to room temperature. This can be done by grinding up the compound with the thermal initiator to obtain a uniform admixture thereof.

The following examples are set out to explain, but expressly not limit, the instant invention. Unless otherwise noted, all parts and percentages are by weight.

Strength properties of adhesive in shear by tension loading (metal to metal) were run in accord with ASTM 1002-64 based on 1" square of lapped area.

**Example 1**

**Preparation of Diisocyanate Adduct**

127.8 g of polypropylene glycol (MW = 725 g/mole) were added dropwise over a 6-hour period to a flask containing 61.4 g of toluene diisocyanate in a nitrogen atmosphere. The reaction was continued with stirring for 4 days at room temperature. The resultant chain-extended isocyanate terminated product will hereinafter be referred to as diisocyanate adduct A.

**Example 2**

To 100 g of a dimethacrylate prepared from diglycidyl ether of bisphenol A and methacrylic acid sold under the tradename "Epocryl-12" by Shell Chemical Co. was added 1 g of triphenyl phosphine. To this mixture was added 129.7 g of diisocyanate adduct A from Example 1 and 4 g of benzopinacol. This reactive mixture was placed in an oven at 80°C for 45 minutes. A urethane-containing, ethylenically unsaturated solid adhesive resulted.

The adhesive was melted at 120°C and applied in a 1" lap to one of two as received cold rolled steel
adherends. The adherends were pressed together and placed in an oven at 160°C for 30 minutes. The average lap shear of 5 test samples was 1,100 psi.

The adhesive was employed in the same manner between two fiber glass and polyester composite adherends. The adherends failed prior to the adhesive bond in the lap shear test.

Example 3

To 100 g of a diacrylate prepared from diglycidyl ether of bisphenol A and acrylic acid sold under the tradename "Epocryl-370" by Shell Chemical Co. was added 0.1 g of dibutyl tin dilaurate. To this mixture was added 137.7 g of diisocyanate adduct A from Example 1 and 4 g of benzopinacol. This reactive mixture was placed in an oven at 50°C for 45 minutes. A urethane-containing, ethylenically unsaturated solid adhesive resulted. The adhesive was melted at 125°C and applied in a 1" lap to one of two as received cold-rolled steel adherends. The adherends were pressed together and placed in an oven at 160°C for 30 minutes. The average lap shear of 5 test samples was 700 psi.

The adhesive was employed in the same manner between two fiber glass and polyester composite adherends. The average lap shear of 5 test samples was 800 psi.

Example 4

To 100 g of the adhesive from Example 2 was added 50 g of Standard-03 iron powder supplied by EMAbond Co. A piece of the adhesive mixture, enough to fill a 1/2" overlap between 2 composite adherends, prepared from glass fiber and polyester, was pressed between the two substrates. The adhesive was cured by the electromagnetic bonding process in a minute. The adherends failed prior to the adhesive bond in the lap shear test.
Example 5

The adhesive of Example 3 was applied to two overlapped composite adherends of the material set out in Example 4 at 125°C. The adhesive was then cured by radio frequency radiation at 200 volts and 0.8 ampere of direct current for 15 minutes. The lap shear strength was 700 psi.
CLAIMS
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A thermoplastic, ethylenically unsaturated linear or cyclic reaction product of a substituted or unsubstituted acrylate ester of an epoxy resin containing at least one hydroxyl group and a polyisocyanate.

2. A thermosettable composition comprising
   (a) a free radical thermal initiator and
   (b) a thermoplastic, ethylenically unsaturated linear or cyclic reaction product of a substituted or unsubstituted acrylate ester of an epoxy resin containing at least one hydroxyl group and a polyisocyanate.

3. A thermoplastic, urethane-containing, ethylenically unsaturated reaction product according to Claim 1 of the general formula:

\[
\begin{align*}
    &\text{CH} = \text{C} - \text{COCH}_2\text{CHOCH}_2\text{R}_4 \quad \text{R}_1 \quad \text{CH} - \text{CH}_2\text{OC} - \text{R}_4 \quad \text{R} - \text{C-OCH}_2\text{OC} - \text{R}_3 \quad \text{C} - \text{C} - \text{NH}_2 \\
    &\text{m} \quad \text{R}_3 \quad \text{R}_1 \quad \text{R}_5 \quad \text{R}_1 \quad \text{NH} - \text{C} - \text{H}_2
\end{align*}
\]

wherein m is 0 or 1; n is 1 to 4; R₂ and R₃ are H or CH₃; R₄ is -CH=CH₂; R₅ is an organic moiety with the valence of p; R₁ is an organic moiety with the valence of q and q is 2 to 4.
4. A process for adhering two substrates which comprises coating at least one of said substrates with a composition comprising
(a) a free radical thermal initiator and
(b) a thermoplastic, ethylenically unsaturated linear or cyclic reaction product of a substituted or unsubstituted acrylate ester of an epoxy resin containing at least one hydroxyl group and a polyisocyanate, contacting the thus coated substrates and heating the thus contacted substrates in the range 100 - 300°C to cause adhesion.

5. The process according to Claim 4 wherein the heating step is carried out by electromagnetic heating.

6. The process according to Claim 5 wherein the electromagnetic heating is by induction heating.

7. The process according to Claim 5 wherein the electromagnetic heating is by dielectric heating.

8. The cured composition of Claim 2 as a sealant.

9. The cured composition of Claim 2 as a coating.

10. The cured composition of Claim 2 as an adhesive.

11. The process of reacting a substituted or unsubstituted acrylate ester of an epoxy resin containing at least one hydroxyl group with a polyisocyanate at a temperature in the range 20-80°C in the presence of 0.1-5 weight percent based on the weight of the reactants of a urethane forming catalyst for a time sufficient to form a thermoplastic, ethylenically unsaturated, urethane containing compound.

12. An adhesive substantially as herein described with reference to Example 2 or Example 3.

13. A process for preparing an adhesive substantially as herein described with reference to Example 2 or Example 3.
14. A process for adhering two substrates substantially as herein described with reference to any one of Examples 2 - 5.

15. The steps or features disclosed herein or any combination thereof.

Dated this 28 day of July 1982.

DAVIES & COLLISON
PATENT ATTORNEYS FOR
W. R. GRACE & CO.
END