

"PHOTOSENSITIVE COMPOSITION AND ELEMENT USEFUL FOR PRODUCING
SOLDERING MASKS"

1 This invention relates to a photosensitive resin
composition and a photosensitive element. More particularly
it relates to a photosensitive resin composition for
forming a protective coating film having excellent
5 characteristics which can be used, for example, for
producing a printed wiring board and for metal precise
processing, and to a photosensitive element comprising a
layer of said composition and a support film supporting
said layer.

10 It is well known that photosensitive elements,
i.e., device comprising a support film and a layer of
substantially dried photosensitive resin composition
formed thereon are used as a photoresist for producing
a printed wiring board. Further, it is also widely
15 known that photosensitive resin compositions having
excellent characteristics which can be used in a soldering
mask, a resist for chemical plating, and the like are
very useful.

 Main objects of a soldering mask are to limit
20 a soldering region at the time of soldering to prevent
soldering bridge and the like; to prevent corrosion of
a naked copper conductor, and to keep electric insulation
between conductors. For these objects, thermosetting
ink such as epoxy resin or the like, or photosetting ink
25 has heretofore been screen-printed. However, in recent

1 years, a wiring density of a printing board has been
increased, and a soldering mask used for it has become
difficult with respect to precision to form by a screen-
printing method. With improvement in wiring density,
5 electric insulation between conductors has come to be
more severely required, and the thickness of a conductor-
protecting film has come to be required to be at least
about 20 μm or more. When a screen-printing method is
used, the average thickness of a resist which can be
10 formed at a time is at most 30 μm , and the thickness of
the thinnest part of a resist formed on the projecting
part of a conductor becomes 10 μm or less inevitably.
When printing is repeated two or three times, a thick
film can be obtained, however it is substantially very
15 difficult with respect to printing precision and because
of complication of processes. Therefore, the advent of
a photosensitive element for forming a soldering mask
is desired. Photosensitive elements in which the thick-
ness of a layer of a photosensitive resin composition
20 is 20 μm or more are useful. Since the thickness of a
conductor in most printed wiring is 18 μm or more,
photosensitive elements in which the thickness of a layer
of a photosensitive resin is 40 μm or more are particularly
useful.

25 In general, photosensitive elements for etching
or electrolytic plating which are called photosensitive
dry films and used for forming a conductor pattern of a
printed wiring board are not sufficient in heat resistance,

1 and hence cannot be used for forming a soldering mask.

Accordingly, there have been put forward many proposals on a photosensitive resin composition for a photosensitive element good in heat resistance which
5 can be used for forming a soldering mask (for example, Japanese Patent Appln. Kokai (Laid-Open) No. 56018/78 (U.S. Patent Appln. Serial No. 735,979 filed October 27, 1976), Japanese Patent Appln. Kokoku (Post-Exam Publ'n) No. 43,092/77 and Japanese Patent Appln. Kokoku (Post-
10 Exam. Publ'n) No. 44,346/78 (U.S. Patent Appln. Serial No. 782,378 filed March 29, 1977). The photosensitive resin compositions in these proposals are excellent in heat resistance which is one of the objects of the proposals, however when a thick protective film of 40 μ m
15 or more in thickness is formed from the compositions, the film cracks within 5 cycles in a thermal shock test holding at 125°C then holding at -65°C repeatedly (MIL-STD-202E method 107D condition B). The thicker the film becomes, the more seriously the film cracks. This
20 becomes a serious problem when the reliability for a long time of a printed wiring board should be taken into consideration.

Among soldering masks formed by a screen-printing method, there are those which are good in
25 resistance to thermal shock. This is mainly because the thickness of soldering masks formed by a screen-printing method is 10 to 30 μ m. Another reason is that printing ink generally contains a large amount of a filler.

17

- 1 It is well known that the presence of the filler contri-
butes to improvement in the resistance to thermal shock.
However, in the case of a photosensitive element, its
layer of a photosensitive resin composition should
5 substantially be dried before irradiation with actinic
light, and should have any filminess. This means that
the layer of a photosensitive resin composition is
required to surely contain a linear high-molecular com-
pound for endowment with filminess as one of the objects.
10 Therefore, said layer is difficult to be incorporated
with a large amount of a filler in addition to a linear
high-molecular compound, an actinic-light-sensitive
compound and a sensitizer.

Further, the present inventors have done various
15 researches to find that when a layer of a photosensitive
resin composition of a photosensitive element is in-
corporated with about 10% by weight of a filler, the
element gives a soldering mask improved in resistance to
thermal shock but is deteriorated in soldering-heat-
20 resistance which is one of the main characteristics of
the mask, and hence is not practical.

As compounds used in photosetting ink for
screen printing, various urethane acrylate compounds or
urethane methacrylate compounds (hereinafter referred
25 to as "urethane (meth)acrylate compounds") have been
proposed as those which are excellent in heat resistance.
However, great difficulty is raised when these compounds
are used not in photosetting ink but in the photosensitive

1 element usually accompanied by imagewise exposure and
development which is an object of this invention. A
first difficulty is that many of the proposed urethane
(meth)acrylate compounds are not or very poorly miscible
5 with linear high-molecular compounds, particularly vinyl
series copolymeric linear high-molecular compounds. A
second difficulty is that many of the proposed urethane
(meth)acrylate compounds are insoluble in noncombustible
solvents used for the development of a photosensitive
10 element, particularly in 1,1,1-trichloroethane series
solvent which is generally most often used. Urethane
(meth)acrylate compounds free from these difficulties
are disclosed in Japanese Patent Appln Kokoku (Post-Exam
Publn) NO. 15,733/76. However, the compositions disclosed
15 therein cannot be used for forming a soldering mask
because of their insufficiency in flexibility, heat
resistance, and the like.

This invention is to provide a photosensitive
resin composition excellent in heat resistance and
20 resistance to thermal shock which can be used for forming
a soldering mask, and a photosensitive element comprising
a layer of said composition and a support film supporting
said layer.

This invention provides a photosensitive resin
25 composition comprising

- (a) 20 to 75 parts by weight of an urethane diacrylate
compound or an urethane dimethacrylate compound (herein-
after referred to as "urethane di(meth)acrylate compound")

1 obtained by reacting, (i) at least one diisocyanate
compound selected from the group consisting of isophorone
diisocyanate and trimethylhexamethylene diisocyanate,
(ii) a dihydric alcohol and (iii) an acrylic monoester
5 or a methacrylic monoester (hereinafter referred to as
"(meth)acrylic monoester") of a dihydric alcohol,

(b) 20 to 75 parts by weight of a linear high-
molecular (or polymeric) compound having a glass transition
temperature of about 40° to 150°C, and

10 (c) a sensitizer and/or a sensitizer system which
generate free radicals owing to actinic light.

Further, this invention provides a photosensitive
element comprising a layer of the photosensitive resin
composition mentioned above, i.e., comprising (a) 20 to
15 75 parts by weight of a urethane di(meth)acrylate compound
obtained by reacting (i) isophorone diisocyanate and/or
trimethylhexamethylene diisocyanate, (ii) a dihydric
alcohol and (iii) a (meth)acrylic monoester of a dihydric
alcohol, (b) 20 to 75 parts by weight of a linear high-
20 molecular compound having a glass transition temperature
of about 40° to 150°C, and (c) a sensitizer and/or a
sensitizer system which generate free radicals owing to
actinic light; and a support film supporting said layer.

In the attached drawings, Figure 1 shows a
25 copper pattern of test substrates used in Examples;
Figure 2 shows a negative mask for test used in Examples;
Figure 3 is a sketch of an apparatus for producing
photosensitive elements used in Examples; and Figures 4

1 and 5 are cross-sectional views showing examples of the photosensitive elements of this invention.

The photosensitive resin composition of this invention is explained below in detail.

5 The photosensitive resin composition of this invention contains as an indispensable component a urethane di(meth)acrylate compound (a) obtained by reacting (i) at least one diisocyanate compound selected from isophorone diisocyanate and trimethylhexamethylene
10 diisocyanate, (ii) a dihydric alcohol and (iii) a (meth)-acrylic monoester of a dihydric alcohol.

As the diisocyanate compound (i), there may be used isophorone diisocyanate (IPDI) manufactured by, for example, Veba Chemie Co., Ltd. (West Germany), and
15 trimethylhexamethylene diisocyanate (TMDI), which is a mixture of 2,2,4-trimethylhexamethylene diisocyanate and 2,4,4-trimethylhexamethylene diisocyanate. IPDI and TMDI can be used alone or as a mixture thereof.

As the dihydric alcohol of (ii) and that in
20 (iii), there can be used methylene glycol, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, 1,4-butanediol, 1,3-butanediol, 2,3-butanediol, 1,5-pentane-
diol, 1,6-hexanediol, 1,10-decanediol, neopentyl glycol,
25 1,4-cyclohexane dimethanol, bis(2-hydroxyethyl)terephthalate, 2,2-bis(4-hydroxyethoxyphenyl)propane, 2,2-bis-(4-hydroxydiethoxyphenyl)propane, and the like.

As the (meth)acrylic monoester of a dihydric

5 The dihydric alcohol of (ii) and that in (iii) may be the same or different. The obtained urethane di(meth)acrylate can be represented by the following formula:



When the urethane di(meth)acrylate compound of this invention is synthesized, the reaction is usually effected at a temperature from 40° to 100°C, and it is preferable to determine the amounts of the isocyanate compound (i), the dihydric alcohol (ii) and the (meth)-

20 compound (i), the dihydric alcohol (ii) and the (meth)-

1 acrylic monoester of a dihydric alcohol (iii), so as to
effect the reaction so that the isocyanate equivalent
of the diisocyanate compound (i) may be almost equal
to the alcohol equivalent of the sum of the dihydric
5 alcohol (ii) and the (meth)acrylic monoester of a di-
hydric alcohol (iii). However, the isocyanate equivalent
may be a little over or a little below the alcohol
equivalent. When the isocyanate equivalent is a little
over the alcohol equivalent, the excess isocyanate groups
10 are finally reacted with a monohydric alcohol such as
methanol, whereby the free isocyanate groups can be
eliminated.

When the ratio of the alcohol equivalent of
the dihydric alcohol (ii) to be reacted to the alcohol
15 equivalent of the (meth)acrylic monoester of a dihydric
alcohol (iii) is adjusted to 1 (provided that the iso-
cyanate equivalent of the diisocyanate compound to be
reacted is made almost equal to the total alcohol equi-
valent), the numerical average value of n becomes 1.

20 When a dihydric alcohol having a large number
of constituting carbon atoms is used, the formed soldering
mask is improved in resistance to thermal shock but
deteriorated in heat resistance. When a dihydric alcohol
having a small number of constituting carbon atoms is
25 used, the formed soldering mask is further improved in
heat resistance, but lowered in resistance to thermal shock.
The number of the constituting carbon atoms of the
dihydric alcohol of (ii) and that in (iii) is preferably

1 1 to 23. It is possible to improve the lowering in
heat resistance in the case of using a dihydric alcohol
having a large number of constituting carbon atoms.
That is to say, the lowering in heat resistance can be
5 prevented by adjusting the alcohol equivalent of the
dihydric alcohol (ii) to be reacted, so as to be less
than the alcohol equivalent of the (meth)acrylic mono-
ester of a dihydric alcohol (iii) (provided that the
isocyanate equivalent of the diisocyanate compound to
10 be used is made equal to the total alcohol equivalent),
and thereby adjusting the numerical average value of n
so as to be 1 or less.

The deterioration in resistance to thermal
shock in the case of using a dihydric alcohol having a
15 small number of constituting carbon atoms can similarly
be prevented. That is to say, the deterioration in
resistance to thermal shock can be prevented by adjusting
the alcohol equivalent of the dihydric alcohol (ii) to
be reacted, so as to be more than the alcohol equivalent
20 of the (meth)acrylic monoester of a dihydric alcohol
(iii) (provided that the isocyanate equivalent of the
diisocyanate compound to be used is made equal to the
total alcohol equivalent), and thereby adjusting the
numerical average value of n so as to be more than 1.
25 That is to say, when the balance between heat resistance
and resistance to thermal shock is taken into considera-
tion, there is a preferable range of the concentration
of the acryloyl group or the methacryloyl group

1 (hereinafter referred to as "(meth)acryloyl group").

The present inventors have done various researches to find that a soldering mask formed by using a photosensitive resin composition obtained by the use of
5 a urethane di(meth)acrylate compound (mixture) containing (meth)acryloyl groups in an amount of 1×10^{-3} to 4.3×10^{-3} equivalent/g is excellent in balance between the heat resistance and the resistance to thermal shock.

When the resistance to electrolytic corrosion
10 of a printed wiring board in which a conductor is protected by a soldering mask is taken into consideration, dihydric alcohols containing no hydrophilic group such as an ether bond or the like in the residues, for example, 1,4-butanediol, 1,3-butanediol, 1,5-pentanediol, 1,6-
15 hexanediol, 1,4-cyclohexane dimethanol, and the like are preferred as the dihydric alcohol (ii) to be reacted.

The urethane di(meth)acrylate compound content ranges from 20 to 75 parts by weight from a consideration of the heat resistance and the resistance to thermal shock.

20 The photosensitive resin composition of this invention contains as an indispensable component a linear high-molecular compound (b) having a glass transition temperature of about 40° to 150°C .

When the glass transition temperature is lower
25 than about 40°C , the heat-resistance of the formed soldering mask is low. When the glass transition temperature exceeds about 150°C , the miscibility of said compound (b) with the urethane di(meth)acrylate compound

1 is lowered, so that it becomes impossible to form a
layer of the photosensitive resin composition on a
support film or a substrate. As the linear high polymer
of the (b) component, there may be used a thermoplastic
5 polymer disclosed in Japanese Patent Appln Kokoku (Post-
Exam Publn) No. 15,932/66 (U.S. Patent Appln. Serial
No. 274,909 filed April 23, 1963). There may be used,
for example, vinyl series linear polymers or copolymers,
copolyesters, polyamides, vinylidene chloride copolymers,
10 synthetic rubbers, and the like. Vinyl series linear
copolymers are preferred from the viewpoint of miscibility
with the urethane di(meth)acrylate compound and adhesion
between the printed wiring substrate and the layer of
a photosensitive resin composition, though vinyl series
15 homopolymers may be used. As the copolymerization compo-
nent of the linear high-molecular compounds, various
vinyl monomers may be used. Suitable examples of the
vinyl monomers include methyl methacrylate, butyl
methacrylate, ethyl acrylate, styrene, α -methylstyrene,
20 vinyltoluene, 2-hydroxyethyl methacrylate, 2-hydroxy-
propyl methacrylate, 2-hydroxyethyl acrylate, acrylic
acid, methacrylic acid, glycidyl methacrylate, t-butyl-
aminoethyl methacrylate, 2,3-dibromopropyl methacrylate,
3-chloro-2-hydroxypropyl methacrylate, acrylamide,
25 acrylonitrile, and the like.

If the formed soldering mask is required to
be flame-retardent, monomers containing one or more
bromine atoms may be used as the copolymerization

1 component.

The content of the bromine atoms in the linear high-molecular compound is suitably up to 40% by weight, and when it exceeds 40% by weight, there is a tendency
5 that the resistance to thermal shock is lowered. As the monomers containing one or more bromine atoms, tribromophenyl (meth)acrylate (this means tribromophenyl acrylate or tribromophenyl methacrylate; and also used hereinafter) is preferred. When the copolymerized amount
10 of tribromophenyl (meth)acrylate is less than 5% by weight, there is little difference in its effect on the flame retardancy between a compound in which it is copolymerized and a compound in which it is not copolymerized. When the copolymerized amount exceeds 65% by weight,
15 the resistance to thermal shock is lowered. The use of antimony trioxide in the photosensitive resin composition is effective for the flame-retardancy. However, when the antimony trioxide content in the photosensitive resin composition exceeds 5% by weight,
20 there is brought about disadvantageous effects on the heat resistance and the like of the formed soldering mask.

The content of the linear high-molecular compound in the photosensitive resin composition ranges
25 from 20 to 75 parts by weight from the viewpoint of the heat resistance and the resistance to thermal shock.

The photosensitive resin composition of this invention contains as an indispensable component a

1. sensitizer and/or a sensitizer system (c) which generates free radicals owing to actinic light. Examples of the sensitizer include substituted and unsubstituted polynuclear quinones such as 2-ethylanthraquinone, 2-t-butylanthraquinone, octamethylanthraquinone, 1,2-benzanthraquinone, 2,3-diphenylanthraquinone, and the like; ketoaldonyl compounds such as diacetyl, benzyl, and the like; α -ketoaldonyl alcohols and ethers such as benzoin, pivalone, and the like; α -hydrocarbon-substituted aromatic acyloins such as α -phenylbenzoin, α,α -diethoxyacetophenone, and the like; and aromatic ketones such as benzophenone, 4,4'-bisdialkylaminobenzophenone, and the like. These may be used alone or in combination of two or more of them. The term "sensitizer system" used herein refers to a combination of a sensitizer and a sensitizing assistant, and as examples of the combination, there are combination of 2,4,5-triarylimidazole dimer and 2-mercaptobenzoquinazole, leucocrystal violet, tris(4-diethylamino-2-methylphenyl)methane, or the like. There may be used additives which have no photoinitiating property by itself but can constitute a good sensitizer system excellent in photoinitiating property as a whole when used in combination with the above-mentioned materials. The additives are, for example, tertiary amines such as triethanolamine and the like which are used in combination with benzophenone. These sensitizers and/or sensitizer systems are contained preferably in an amount of 0.5 to 10% by weight based on

1 the sum of amounts of the above-mentioned (a) urethane
di(meth)acrylate compound and (b) linear high-molecular
compound.

The photosensitive resin composition of this
5 invention may contain other photopolymerizable unsaturat-
ed compounds. As the other photopolymerizable unsaturated
compounds, there may be exemplified trimethylolpropane
triacylate, pentaerythritol triacylate, tetraethylene-
glycol diacylate, and the like.

10 There may also be used polymerizable unsaturated
compounds disclosed in Japanese Patent Application
Kokai (Laid-Open) No. 56,018/78 (U.S. Patent Appln.
Serial No. 735,979 filed October 27, 1976). However,
the content of these other photopolymerizable unsaturated
15 compounds is preferably 20% by weight or less, particularly
preferably 10% by weight or less based on the total
amounts of the above-mentioned (a) urethane di(meth)-
acrylate compound and (b) linear high-molecular compound
from a consideration of balance between the heat resistance
20 and the resistance to thermal shock. The other photo-
polymerizable unsaturated compounds may be added in
order to improve other characteristics such as the solvent
resistance, the adhesion, and the like, and (meth)acrylic
esters (this means acrylic esters or methacrylic esters;
25 and also used hereinafter) containing a phosphoric acid
group in the molecule are preferable for further improv-
ing the adhesion between the formed soldering mask and
the printed wiring substrate.

1 Examples of the (meth)acrylic esters containing
a phosphoric acid group include PM-1, PM-2, PA-1 and
PA-2 in KAYAMER[®] series manufactured by Nihon Kayaku
Co., Ltd., Phosmer M[®] (acid phosphoxyethyl methacrylate),
5 Phosmer CL[®] (3-chloro-2-acid phosphoxypropyl methacrylate)
manufactured by Fats and Oils Articles Co., Ltd., etc.
The content of these (meth)acrylic esters containing in
the molecule a phosphoric acid group is preferably 0.01
to 5% by weight based on the total amounts of the above-
10 mentioned (a) urethane di(meth)acrylate compound and
(b) linear high-molecular compound.

Further, the photosensitive resin composition
of this invention may contain other secondary components.
The secondary components include thermopolymerization
15 inhibitors, dyes, pigments, coating property improvers,
and the like, and these are selected with the same con-
sideration as in the case of ordinary photosensitive
resin compositions.

Next, the photosensitive element of this inven-
20 tion is explained below in detail.

The photosensitive element of this invention
can be obtained by forming a layer 19 of the photosensi-
tive resin composition explained above in detail on a
support film 18 as shown in Figure 4. The layer of the
25 photosensitive resin composition can be formed on a
support film by a conventional process. For example,
it can be formed by uniformly dissolving the photosensi-
tive resin composition in an organic solvent such as

1 methyl ethyl ketone, toluene, methylene chloride, or
the like (or dispersing it therein when a flame-
retarding assistant such as antimony trioxide, a pigment,
or the like is used), applying the resulting solution onto
5 said support film by a knife coating method, a roll
coating method, or the like, and then drying the solution.
The amount of the remaining solvent in the photosensitive
layer is limited to preferably 2% by weight or less,
particularly preferably 1% by weight or less.

10 It is preferable that the support film used in
this invention has heat resistance and solvent resistance
which are necessary at the time of the production of
the photosensitive element. The support film may be
either pervious or not pervious to actinic light. Pre-
15 ferable examples of the support film include well-known
films such as a polyester film, a polypropylene film,
a polyimide film, a polyamide-imide film, a polystyrene
film and the like.

When a long photosensitive element is produced,
20 said element is wound into a roll in the final step of
the production. In this case, the layer of the photo-
sensitive resin composition can be prevented from
adhering to the back side of the support film in winding
the element into a roll, by using a support film whose
25 back side has been treated by a method well known in
the field of a pressure-sensitive sticking tape and the
like. It is preferable to laminate a covering film 20
as shown in Figure 5 which can be peeled off on the layer

1 of a photosensitive resin composition of said element,
for the same object as above, an object of preventing
the adhesion of dust, etc.

As examples of the covering film which can be
5 peeled off, there are a polyethylene film, a polypropylene
film, a Teflon^(RTM) film, surface-treated paper, and the like,
and any covering film may be used so long as adhesion
between it and the layer of a photosensitive resin
composition is lower than adhesion between the layer of
10 a photosensitive resin composition and the support film
when it is peeled off.

The thickness of the layer of a photosensitive
resin composition constituting the photosensitive element
of this invention is preferably 20 to 200 μm for keeping
15 high electric insulation between the conductors of a
printing wiring substrate in which the layer is used,
and from the viewpoint of the resolution of the formed
soldering mask pattern.

Next, examples of a method for using the photo-
20 sensitive element of this invention are explained below.

The photosensitive element of this invention
is easy to laminate on a substrate. That is to say,
it is laminated, with heating under pressure, as such
when it has no covering film, or after or while peeling
25 off its covering film when it has a covering film. The
lamination with heating under pressure can be carried
out by means of a laminater which is well known to printed
wiring board manufacturers. When the substrate has

1 unevenness of 10 μ m or more as in the case of a printed
wiring board in which conductor-wiring lines have been
formed, it is preferable to carry out the lamination
under reduced pressure or in vacuo.

5 As an apparatus for such lamination, there is,
for example, a laminating apparatus disclosed in Japanese
Patent Appln Kokoku (Post-Exam Publn) No. 31,670/78
(U.S.P. 4,101,364) or Japanese Patent Appln Kokoku
(Post-Exam Publn) No. 13,341/80 (U.S.P. 4,127,436).

10 The exposure and the development treatment
after the lamination can be carried out by a conventional
method. That is to say, when the support film is not
pervious to actinic light, the support film is peeled
off and thereafter the imagewise exposure is carried out
15 through a negative mask by using a light source such as
a high pressure mercury arc lamp, an ultra-high pressure
mercury lamp, or the like. Heat treatment at 50° to 100°C
before and after the exposure is preferable for increasing
adhesion between the substrate and the photosensitive
20 resin layer.

As the developing solution, a solvent such as
1,1,1-trichloroethane or the like is used. It is
preferable for safety to use a noncombustible solvent.

The imagewise protective coating film obtained
25 in the manner described above is an anti-corrosive
coating film for usual etching, metal plating, and the
like, and it becomes a protective coating film having
more excellent characteristics by heat treatment at

1. 80° to 200°C and exposure to actinic light after the development. As to the order of the heat treatment and the exposure to actinic light after the development, either may be the first, and each of them may be carried
5 out by dividing into several steps. The protective coating film obtained by heat treatment and exposure to actinic light after the development is sufficiently resistant to organic solvents such as trichlene, methyl ethyl ketone, isopropyl alcohol, toluene, and the like
10 and is resistant also to an acidic aqueous solution and an aqueous alkali solution. Furthermore, it is excellent in heat resistance and resistance to thermal shock, and hence is suitable as a permanent protective coating film such as a soldering mask and the like which is required
15 to have reliability for a long time.

The protective coating film having as excellent characteristics as in the above can also be obtained by directly coating a substrate with a solution of the photosensitive resin composition of this invention by
20 a dip-coating method, a flow-coating method, or the like, drying the solvent, imagewise exposing the coating through a negative mask in the same manner as in the case of the above-mentioned photosensitive element, directly or after laminating a film pervious to actinic
25 light on the coating, carrying out development, and then carrying out heat treatment and exposure to actinic light.

Since a coating film formed by using the

1 photosensitive resin composition or the photosensitive
element of this invention has excellent chemical and
physical characteristics as mentioned above, it is used
also in printing materials, plastics reliefs, and the
5 like.

Next, this invention is further explained below
referring to Examples, in which all parts and percents
are by weight unless otherwise provided.

Example 1

10 a) Synthesis of a urethane diacrylate compound

A	Trimethylhexamethylene diisocyanate	1,680 parts (16 equivalents)
	Toluene (solvent)	1,200 parts
	Di-n-butyl tin dilaurate (catalyst)	1 part
B	1,6-Hexanediol	472 parts (8 equivalents)
C	2-Hydroxyethyl acrylate	928 parts (8 equivalents)
	Toluene (solvent)	88 parts
	Hydroquinone (thermopolymerization inhibitor)	0.4 part
D	Methanol (stopping agent)	32 parts

The ingredients as mentioned above were placed
in a reactor having a capacity of about 5 liters equipped
with a thermometer, a stirrer, a condenser, a nitrogen-
gas-introducing tube and a dropper which could be heated

1 and cooled, and then ingredient A was heated to 60°C
with stirring. The ingredient B was uniformly added
dropwise to the ingredient A in the reactor over a
period of about 3 hours while maintaining the reaction
5 temperature at 55 to 65°C. After the addition of the
ingredient B, the resulting mixture was maintained at
a temperature of 55° to 65°C for about 2 hours, after
which the ingredient C was uniformly added thereto drop-
wise at a temperature of about 55° to 65°C over a period
10 of about 3 hours. After the addition of the ingredient
C, the reaction temperature was gradually raised to 80°C
over a period of about 5 hours. Thereafter, the tempera-
ture was lowered to 60°C, after which the ingredient D
was added to the reaction mixture, and the thus obtained
15 mixture was continuously stirred for about 1 hour to
give a solution (I) of a urethane diacrylate compound
which contained 70% of nonvolatile matters.

b) Production of a photosensitive element

The solution (I) of a urethane diacrylate compound obtained in the manner described above	70 parts (49 parts in terms of non-volatile matters)
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Methyl methacrylate-methacrylic acid-tetrahydrofurfuryl methacrylate (78/2/20; weight ratio) copolymer (having a molecular weight of about 150,000 and a glass transition temperature of about 95°C)	47 parts
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Benzophenone	2.7 parts
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Michler's ketone	0.3 parts
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p-Methoxyphenol	0.1 part
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Crystal violet	0.1 part
Methyl ethyl ketone	80 parts

1 A solution of a photosensitive resin composition was prepared by mixing the above-mentioned ingredients and then applied to a polyimide film of about 50 μm in thickness, and then dried at room temperature for 5 20 minutes, at 80°C for 10 minutes and then at 105°C for 5 minutes to obtain a photosensitive element in which the thickness of the layer of the photosensitive resin composition was about 60 μm .

c) Formation of a soldering mask

10 Six test substrates having a copper pattern shown in Figure 1 were obtained by imagewise etching of a laminate faced with glass epoxy copper in which the thickness of its substrate was 1.6 mm and the thickness of the copper foil was 1.8 μm . In Figure 1, numeral 1 15 shows a copper pattern part; numeral 2 shows an exposed part of the substrate; and the unit of the figures is mm. The photosensitive element obtained in above b) was laminated on each of the test substrates by using an A-500 type laminater manufactured by Akebono Industry 20 Co., Ltd. After the lamination, the polyimide film as a support film was peeled off, and the test substrates were exposed at 900 mJ/cm^2 by means of a Phenix 3000 type exposing machine manufactured by ORC Factory Co., Ltd. by using a negative mask for test shown in Figure 2.

1 In Figure 2, numeral 3 shows an opaque part of the
negative mask; numeral 4 shows a transparent part of
the negative mask; and the unit of the figures is mm.
After the exposure, the test substrates were allowed to
5 stand for 30 minutes, and then subjected to spray
development at 20°C for 90 seconds by using 1,1,1-
trichloroethane. After the development, they were heated
and dried at 80°C for 10 minutes and then irradiated at
2.5 J/cm² by using an ultraviolet light irradiating
10 equipment manufactured by Toshiba Denzai Co., Ltd.

Thereafter, it was heat-treated at 150°C for
30 minutes.

Four of the six test substrates on which a
protective coating film was thus formed were immersed
15 in isopropanol, toluene, trichlene, or a 10% aqueous
hydrochloric acid solution, all at 25°C, respectively,
for 10 minutes to find that the formed protective coating
film underwent no change.

When another one of the test substrates was
20 immersed in a soldering bath at 255°C to 265°C for 30
seconds, its protective coating film was so stable
that it did neither crack nor peel off from the sub-
strate, and therefore it was found to be sufficiently
usable as a soldering mask.

25 The remaining one test substitute was subjected
to soldering treatment in a soldering bath at 255° to 265°C
for 3 seconds by using a rosin series flux A-226
(manufactured by Tamura Kaken Co., Ltd.), and then

- 1 subjected to the thermal shock test of 50 cycles under
MIL-STD-202E method 107D condition B (-65°C for 30
minutes $\pm$ ordinary temperature for 5 minutes or
less $\pm$ 125°C for 30 minutes) to find that its
5 protective coating film did not crack and was greatly
excellent in reliability for a long time.

Example 2

a) Synthesis of a urethane diacrylate compound

A	Trimethylhexamethylene diisocyanate	1,680 parts (16 equivalents)
	Toluene	800 parts
	Di-n-butyl tin dilaurate (catalyst)	1 part
B	1,4-Cyclohexane dimethanol	360 parts (5 equivalents)
	2-Hydroxyethyl acrylate	348 parts (3 equivalents)
	Methyl ethyl ketone (solvent)	520 parts
C	2-Hydroxyethyl acrylate	928 parts (8 equivalents)
	Toluene (solvent)	80 parts
	p-Methoxyphenol (thermopolymerization inhibitor)	0.3 part
D	Ethanol (stopping agent)	23 parts

A solution of a urethane acrylate compound was
10 obtained according to the above recipe in the same manner

- 1 as in Example 1-a). Thereafter, it was dried under reduced pressure to obtain a viscous urethane diacrylate compound (II).

b) Production of a photosensitive element

The urethane diacrylate compound (II) obtained by the above-mentioned process	40 parts
Methyl methacrylate-methyl acrylate-2-hydroxyethyl methacrylate-acrylonitrile (80/10/5/5 weight ratio) copolymer (having a molecular weight of about 100,000 and a glass transition temperature of about 90°C)	57 parts
Benzophenone	2.7 parts
Michler's ketone	0.3 part
p-Methoxyphenol	0.1 part
Victoria pure blue	0.05 part
Methyl ethyl ketone	80 parts
Toluene	40 parts

- 5 A solution 10 of a photosensitive resin composition prepared from the above recipe was uniformly applied to a polyethylene terephthalate film 16 of 25 μm in thickness by using an apparatus shown in Figure 3, and then dried in a hot-air convection dryer
- 10 11 at 80° to 100°C for about 10 minutes. The thickness after drying of the layer of the photosensitive resin composition was about 100 μm . A polyethylene film 17 of about 25 μm in thickness was stuck as a covering film

1 on the layer of the photosensitive resin composition
as shown in Figure 3.

In Figure 3, numeral 5 shows a polyethylene
terephthalate film delivering roll, numerals 6, 7 and 8
5 rolls, numeral 9 a knife, numeral 12 a polyethylene film
delivering roll, numerals 13 and 14 rolls and numeral 15
a photosensitive element winding roll.

c) Formation of a soldering mask

The photosensitive element obtained in the
10 above was laminated with heating under pressure on
printed wiring boards for test (having a glass epoxy
substrate and a thickness of 1.6 mm) in which a copper
pattern (copper thickness: about 70 μ m) shown in Figure
1 had been formed, by using a vacuum laminater manu-
15 factured by Hitachi Chemical Co., Ltd. (degree
of vacuum: 30 mmHg, lamination temperature: 100°C,
lamination speed: 2 m/min.). After the lamination,
the printed wiring boards were heated at 60°C for 5
minutes, allowed to stand at room temperature for 3
20 hours, and then exposed at 150 mJ/cm² through a negative
mask for test shown in Figure 2, as in Example 1-c).

After the exposure, the boards were heated
at 80°C for 5 minutes and then allowed to stand at room
temperature for 20 minutes, after which the support film
25 was peeled off, and the boards were subjected to spray
development at 20°C for 150 seconds by using 1,1,1-
trichloroethane.

After the development, the boards were heated

- 1 and dried at 80°C for 10 minutes, irradiated with ultra-violet light at 3.0 J/cm², and then heat-treated at 130°C for 2 hours.

The test substrates on which a protective
5 coating film had been formed in the manner described above were subjected to an immersion test in isopropanol, toluene, trichlene or a 10% aqueous hydrochloric acid solution all at 25°C, respectively, for 10 minutes in the same manner as in Example 1-c) to find that the formed
10 protective coating film underwent no change..

When an immersion test was carried out in a soldering bath at 255° to 265°C for 30 seconds, the protective coating film showed no defect and was excellent in heat resistance. Further, in the thermal shock test
15 of 50 cycles under MIL-STD-202E method 107D condition B after the same soldering treatment as in Example 1-c), the formed coating film did not crack.

Example 3

The urethane diacrylate compound (II) obtained in Example 2-a)	60 parts
Methyl methacrylate-methacrylic acid (98/2 weight ratio) copolymer (having a molecular weight of about 100,000 and a glass transition temperature of about 105°C)	37 parts
Benzophenone	2.7 parts
Michler's ketone	0.3 part
p-Methoxyphenol	0.1 part

Victoria pure blue	0.02 part
Methyl ethyl ketone	60 parts
Toluene	70 parts

1 By the use of a solution of a photosensitive resin composition prepared from the above recipe, a photosensitive element in which the thickness of a layer of the photosensitive resin composition was about 80 μm

5 was obtained by using an apparatus shown in Figure 3, as in Example 2-b). The photosensitive element was laminated under reduced pressure in the same manner as in Example 2-c) on printed wiring boards for test on which a copper pattern (copper thickness: about 50 μm) shown in

10 Figure 1 had been formed. Further, the same treatment as in Example 2-c) was carried out to form an imagewise protective coating film on said test substrates. The formed protective coating film showed no defect in the immersion test in isopropanol, toluene, trichlene,

15 methyl ethyl ketone, a 10% aqueous hydrochloric acid solution or a 10% aqueous NaOH solution all at 25°C, respectively, for 10 minutes, and was so excellent in heat resistance that it did neither crack nor peel off from the substrate in the immersion test for 30 seconds

20 in a soldering bath at 255° to 265°C. Further, when the test substrate was subjected to the same soldering treatment as in Example 1-c) and then subjected to the thermal shock test of 50 cycles under MIL-STD-202E method 107D condition B, the protective coating film did not crack.

1 Comparative Example 1

The same procedures as in Example 2-b) and Example 2-c) were carried out except that trimethylolpropane triacrylate was substituted for the urethane diacrylate compound (II) in Example 2-b). The finally obtained protective coating film partly peeled off from the substrate in the immersion test in a soldering bath at 255° to 265°C for 30 seconds. After the same soldering treatment as in Example 1-c), the protective coating film cracked within 5 cycles in the thermal shock test under MIL-STD-202E method 107D condition B.

Comparative Example 2

The same procedure as in Example 3 was carried out except that 20 parts of pentaerythritol triacrylate and 40 parts of a di-(3-acryloxy-2-hydroxypropyl)ester of bisphenol A were substituted for 60 parts of the urethane diacrylate compound (II) in Example 3. After the same soldering treatment as in Example 1-c), the finally obtained protective coating film cracked within 5 cycles in the thermal shock test under MIL-STD-202E method 107D condition B. A part of the protective coating film was about to peel off from the substrate in the immersion test for 10 minutes in a 10% aqueous hydrochloric acid solution.

25 Comparative Example 3

Trimethylolpropane triacrylate 30 parts

Polypropylene glycol (having an average molecular weight of 1,000) diacrylate	10 parts
Methyl methacrylate-methacrylic acid-tetrahydrofurfuryl methacrylate (78/2/20 weight ratio) copolymer (having a molecular weight of about 150,000 and a glass transition temperature of about 95°C)	50 parts
Benzophenone	2.7 parts
Michler's ketone	0.3 part
p-Methoxyphenol	0.5 part
Methyl ethyl ketone	200 parts

- 1 The same procedure as in Example 3 was carried out except that a solution of a photosensitive resin composition prepared from the above recipe was used. The finally obtained protective coating film was excellent
- 5 in solvent resistance and heat resistance, but cracked within 10 cycles in the thermal shock test under MIL-STD-202E method 107D condition B after the same soldering treatment as in Example 1-c).

Example 4

a) Synthesis of a urethane diacrylate compound

A Trimethylhexamethylene diisocyanate	1,680 parts (16 equivalents)
Toluene (solvent)	1,200 parts
Di-n-butyl tin dilaurate (catalyst)	1 part

B	Triethylene glycol	600 parts (8 equivalents)
C	2-Hydroxypropyl acrylate	1,040 parts (8 equivalents)
	Toluene (solvent)	190 parts
	Hydroquinone (thermopolymerization inhibitor)	0.4 part
D	Methanol (stopping agent)	32 parts

- 1 A solution of a urethane diacrylate compound
was obtained according to the above recipe in the same
manner as in Example 1-a). Thereafter, the solution
was dried under reduced pressure to obtain a viscous
5 urethane diacrylate compound (III).

b) Production of a photosensitive element and forma-
tion of a soldering mask

The urethane diacrylate com- pound (III) obtained in the manner described above	60 parts
Methyl methacrylate-meth- acrylic acid-tribromophenyl acrylate (38/2/60 weight ratio) copolymer (having a molecular weight of about 120,000, a glass transition temperature of about 120°C and a bromine content of 37% by weight)	37 parts
Benzophenone	2.7 parts
4,4'-Bis(diethylamino)- benzophenone	0.3 part
2,2'-methylenebis(4-ethyl- 6-t-butylphenol)	0.3 part

Victoria pure blue	0.02 part
Methyl ethyl ketone	100 parts
Toluene	50 parts

1 The same procedures as in Example 2-b) and
Example 2-c) were followed, with the exception that a
solution of a photosensitive resin composition prepared
from the above recipe was used. The finally obtained
5 protective coating film showed no defect in the immersion
test for 10 minutes in a 10% aqueous hydrochloric acid
solution, and underwent no change such as peeling-off
and cracking when immersed in a soldering bath at 255°
to 265°C for 30 seconds. After the same soldering treat-
10 ment as in Example 1-c), the protective coating film
did not crack in the thermal shock test of 50 cycles
under MIL-STD-202E method 107D conditon B. A protective
coating film was formed by the same procedure as in the
above on the whole surface of a substrate of 0.8 mm
15 in thickness of a printing wiring substrate MCL-E-68
(UL flame-retardancy grade 94V-0) manufactured by
Hitachi Chemical Co., Ltd. This protective coating
film satisfied the standards of 94V-1 of UL.

Example 5

a) Synthesis of a urethane diacrylate compound

A Trimethylhexamethylene diisocyanate	1,680 parts (16 equivalents)
Toluene (solvent)	1,000 parts

	Di-n-butyl tin dilaurate (catalyst)	1 part
B	Ethylene glycol	310 parts (10 equivalents)
C	2-Hydroxyethyl acrylate	696 parts (6 equivalents)
	Toluene (solvent)	150 parts
	Hydroquinone (thermopolymerization inhibitor)	0.3 part
D	Methanol (stopping agent)	32 parts

- 1 A solution of a urethane diacrylate compound was obtained according to the above recipe in the same manner as in Example 1-a). Thereafter, it was dried under reduced pressure to obtain a viscous urethane
- 5 diacrylate compound (IV).

b) Production of a photosensitive element and formation of a soldering mask

The urethane diacrylate compound (IV) obtained in the manner described above

50 parts

Methyl methacrylate-methyl acrylate-acrylic acid-tetrahydrofurfuryl methacrylate-tribromophenyl acrylate (40/23/2/10/25 weight ratio) copolymer (having a molecular weight of about 80,000, a glass transition temperature of about 75°C and a bromine content of 15% by weight)

47 parts

Benzophenone

2.7 parts

Michler's ketone

0.3 part

2,2'-Methylenebis(4-methyl-6-t-butylphenol)	0.5 part
Victoria pure blue	0.02 part
Methyl ethyl ketone	100 parts
Toluene	50 parts

- 1 The same procedures as in Example 2-b) and Example 2-c) were followed, with the exception that a solution of a photosensitive resin composition prepared from the above recipe was used. The finally obtained
- 5 protective coating film showed no defect in the immersion test for 10 minutes in isopropanol, toluene, trichlene, or a 10% aqueous hydrochloric acid solution, and underwent no change such as peeling-off and cracking when immersed in a soldering bath at 255° to 265°C for 30 seconds.
- 10 After the same soldering treatment as in Example 1-c), the protective coating film did not crack in the thermal shock test of 50 cycles under MIL-STD-202E method 107D condition B. A protective coating film was formed by
- 15 the same procedure as in the above on the whole surface of a substrate of 1.6 mm in thickness of a printed wiring board MCL-E-68 manufactured by Hitachi Chemical Co., Ltd. This protective coating film satisfied the standards of 94V-1 of UL.

Example 6

- 20 The same procedure as in Example 5-b) was followed, with the exception that 1 part of antimony

1 trioxide was additionally incorporated into the solution
of the photosensitive resin composition in Example 5-b).
The finally obtained protective coating film was as
good as in Example 5-b) in solvent resistance, heat
5 resistance and resistance to thermal shock. A protective
coating film was formed by the same procedure as in the
above on the whole surface of a substrate of 1.6 mm in
thickness of a printed wiring substrate MCL-E-68 manu-
factured by Hitachi Chemical Co., Ltd. This protective
10 coating film satisfied the standards of 94V-0 of UL.

Example 7

a) Synthesis of a urethane dimethacrylate compound

A	Trimethylhexamethylene diisocyanate	1,680 parts (16 equivalents)
	Toluene (solvent)	1,000 parts
	Di-n-butyl tin dilaurate (catalyst)	1 part
B	1,4-Butanediol	360 parts (8 equivalents)
C	2-Hydroxyethyl methacrylate	1,040 parts (8 equivalents)
	Toluene (solvent)	280 parts
	Hydroquinone (thermopolymerization inhibitor)	0.3 part
D	Methanol (stopping agent)	32 parts

A solution of a urethane dimethacrylate compound
was obtained according to the above recipe in the same

1 manner as in Example 1-a). Thereafter, it was dried under reduced pressure to obtain a viscous urethane dimethacrylate compound (V).

b) Production of a photosensitive element and forma-
5 tion of a soldering mask

The urethane dimethacrylate com- 40 parts
pound (V) obtained in the
manner described above

Methyl methacrylate-meth- 57 parts
acrylic acid-tetrafurfuryl
methacrylate-acrylonitrile-
tribromophenyl acrylate
(43/2/20/5/30 weight ratio)
copolymer (having a molecular
weight of about 150,000, a
glass transition temperature
of about 100°C and a bromine
content of 18% by weight)

Benzophenone 2.7 parts

Michler's ketone 0.3 part

p-Methoxyphenol 0.05 part

Victoria pure blue 0.05 part

Toluene 150 parts

The same procedures as in Example 2-b) and
Example 2-c) were followed, with the exception that a
solution of a photosensitive resin composition prepared
from the above recipe was used. The finally obtained
10 protective coating film showed no defect in the immersion
test for 10 minutes in isopropanol, toluene, trichlene
or a 10% aqueous hydrochloric acid solution, and underwent
no change such as peeling-off and cracking when immersed
in a soldering bath at 255° to 265°C for 30 seconds.

- 1 After the same soldering treatment as in Example 1-c),
it did not crack in the thermal shock test of 50 cycles
under MIL-STD-202E method 107D condition B. A protective
coating film was formed by the same procedure as above
- 5 on the whole surface of a substrate of 1.6 mm in thick-
ness of a printed wiring substrate MCL-E-68 manufactured
by Hitachi Chemical Co., Ltd. This protective coating
film satisfied the standards of 94V-1 of UL.

Example 8

- 10 a) Synthesis of a urethane diacrylate compound
- | | | |
|---|--|---------------------------------|
| A | Trimethylhexamethylene diisocyanate | 1,680 parts
(16 equivalents) |
| | Toluene (solvent) | 1,000 parts |
| | Di-n-butyl tin dilaurate (catalyst) | 1 part |
| B | 1,4-Cyclohexane-dimethanol | 216 parts
(3 equivalents) |
| | Tetraethylene glycol | 291 parts
(3 equivalents) |
| | Methyl ethyl ketone (solvent) | 200 parts |
| C | 2-Hydroxyethyl acrylate | 1,160 parts
(10 equivalents) |
| | Toluene (solvent) | 200 parts |
| | p-Methoxyphenol (thermopolymerization inhibitor) | 0.2 part |
| D | Methanol | 32 parts |

52

- 1 A solution of a urethane diacrylate compound was obtained according to the above recipe in the same manner as in Example 1-a). Thereafter, it was dried under reduced pressure to obtain a viscous urethane
- 5 diacrylate compound (VI).

b) Production of a photosensitive element

The urethane diacrylate compound (VI) obtained in the manner described above	47 parts
Methyl methacrylate-methyl acrylate-acrylic acid-tetrahydrofurfuryl methacrylate-2-hydroxyethyl methacrylate-tribromophenyl acrylate (43/10/2/5/5/35 weight ratio) copolymer (having a molecular weight of about 150,000, a glass transition temperature of about 90°C and a bromine content of 22% by weight)	50 parts
Benzophenone	2.7 parts
Michler's ketone	0.3 part
p-Methoxyphenol	0.05 part
Victoria pure blue	0.02 part
KAYAMER PA-2 (manufactured by Nihon Kayaku Co., Ltd.: divalent acrylate containing a phosphoric acid group)	0.1 part
Methyl ethyl ketone	50 parts
Toluene	100 parts

By the use of a solution of a photosensitive resin composition prepared from the above recipe, a photosensitive element in which the thickness of a layer

1 of the photosensitive resin composition was about 50 μm was obtained by using an apparatus shown in Figure 3, as in Example 2-b).

c) Formation of a soldering mask

5 The photosensitive element obtained in the above was laminated under reduced pressure in the same manner as in Example 2-c) on a printed wiring boards for test on which a copper pattern (copper thickness: about 18 μm) shown in Figure 1 had been formed. After
10 the lamination, the printed wiring boards were allowed to stand at room temperature for 3 hours, and then exposed at 200 mJ/cm^2 through a negative mask for test shown in Figure 2, as in Example 1-c). After the exposure, the boards were heated at 80°C for 5 minutes and then allowed
15 to cool at room temperature for 20 minutes, after which the support film was peeled off, and the boards were subjected to spray development at 20°C for 70 seconds by using 1,1,1-trichloroethane. After the development, the boards were heated and dried at 80°C for 30 minutes,
20 and further heated at 120°C for 30 minutes and then at 150°C for 30 minutes. The heated boards were allowed to cool at room temperature for 10 minutes, irradiated with ultraviolet light at 10 J/cm^2 , and then heat-treated at 130°C for 2 hours.

25 The test substrates on which a protective coating film had been formed in the manner described above were subjected to the immersion test for 10 minutes

1. in isopropanol, toluene, trichlene or a 10% aqueous hydrochloric acid solution all at 25°C in the same manner as in Example 1-c), to find that the protective coating film showed no defect. The protective coating film
5 did not peel off in the immersion test for 30 minutes in a soldering bath at 255° to 265°C and hence was good in heat resistance. After the same soldering treatment as in Example 1-c), the film did not crack in the thermal shock test of 50 cycles under MIL-STD-202E method 107D
10 condition B. The protective coating film was so excellent in adhesion that it did not peel off in a cross-cutting test. A protective coating film was formed by the same procedure as in the above on the whole surface of a substrate of 0.8 mm in thickness of a printed wiring
15 substrate MCL-E-68 manufactured by Hitachi Chemical Co., Ltd. This protective coating film satisfied the standards of 94V-1 of UL.

Comparative Example 4

A urethane diacrylate compound was synthesized
20 in the same manner as in Example 1-a), except that 1,344 parts (16 equivalents) of hexamethylene diisocyanate was substituted for 1,680 parts (16 equivalents) of trimethylhexamethylene diisocyanate in Example 1-a).

The produced urethane diacrylate compound (VII)
25 was insoluble in toluene, the reaction solvent, and separated as wax just as it was produced. The obtained urethane diacrylate compound (VII) was slightly soluble in

- 1 methyl ethyl ketone and 1,1,1-trichloroethane, and soluble in acetone and chloroform.

The obtained urethane diacrylate compound (VII)	50 parts
The copolymer used in Example 1-b)	47 parts
Benzophenone	2.7 parts
Michler's ketone	0.3 part
p-Methoxyphenol	0.05 part
Victoria pure blue	0.02 part
Acetone	50 parts
Chloroform	100 parts

A solution of a photosensitive resin composition prepared from the above recipe was applied to a poly-
5 ethylene terephthalate film by using an apparatus shown in Figure 3, as in Example 2-b), and then dried in hot air to find that the urethane diacrylate compound (VII) and the copolymer separated from each other just as the solvent was dried, so that no desirable photosensitive
10 element could be obtained. When any of the copolymers used in Examples 2 to 8 was used, the miscibility was as low as in the above, and no desirable photosensitive element could be obtained.

Example 9

- a) Synthesis of a urethane diacrylate compound

A Isophorone diisocyanate	1,776 parts (16 equivalents)
---------------------------	---------------------------------

	Toluene (solvent)	1,200 parts
	Di-n-butyl tin dilaurate (catalyst)	1 part
B	1,6-Hexanediol	472 parts (8 equivalents)
C	2-Hydroxyethyl acrylate	928 parts (8 equivalents)
	Toluene (solvent)	129 parts
	Hydroquinone (thermopolymerization inhibitor)	0.4 part
D	Methanol (stopping agent)	32 parts

- 1 The ingredient A was placed in a reactor having a capacity of about 5 liters equipped with a thermometer, a stirrer, a condenser, a nitrogen-gas-introducing tube and a dropper which could be heated and
- 5 cooled, and then A was heated to 60°C with stirring. B was uniformly added dropwise to A in the reactor over a period of about 3 hours while maintaining the reaction temperature at 55° to 65°C. After the addition of B, the resulting mixture was maintained at a temperature
- 10 of 55° to 65°C for about 2 hours, after which C was uniformly added thereto dropwise at a temperature of about 55° to 65°C over a period of about 3 hours. After the addition of C, the reaction temperature was gradually raised to 80°C over a period of about 5 hours.
- 15 Thereafter, the temperature was lowered to 60°C, after which D was added to the reaction mixture, and the thus obtained mixture was continuously stirred for about

57

1. 1 hour. A solution (VIII) of a urethane diacrylate compound which contained 70% of nonvolatile matters was thus obtained.

b) Production of a photosensitive element

The solution (VIII) of a urethane diacrylate compound obtained in the manner described above	70 parts (49 parts in terms of non-volatile matters)
--	---

Methyl methacrylate-methacrylic acid-tetrahydrofurfuryl methacrylate (78/2/20: weight ratio) copolymer (having a molecular weight of about 150,000 and a glass transition temperature of about 95°C)	47 parts
--	----------

2-Ethylanthraquinone -	4 parts
------------------------	---------

p-Methoxyphenol	0.1 part
-----------------	----------

Crystal violet	0.1 part
----------------	----------

Methyl ethyl ketone	80 parts
---------------------	----------

5 A solution of a photosensitive resin composition was prepared according to the above recipe, applied to a polyimide film of about 50 μm in thickness, and dried at room temperature for 20 minutes, at 80°C for 10 minutes and then at 105°C for 5 minutes to obtain a photosensitive element in which the thickness of a layer of the photosensitive resin composition was about 60 μm .

c) Formation of a soldering mask

Six test substrates having a copper pattern shown in Figure 1 were obtained by imagewisely etching a laminate faced with glass epoxy copper in which the

1 thickness of its substrate was 1.6 mm and the thickness
of the copper foil was 18 μm . In Figure 1, 1 shows a
copper pattern part and 2 shows an exposed part of the
substrate, and the unit of the figures is mm.

5 The photosensitive element obtained in above b)
was laminated on each of the test substrates by using an
A-500 type laminater manufactured by Akebono Industry
Co., Ltd. After the lamination, the polyimide film as
a support film was peeled off, and the test substrates
10 were exposed at 900 mJ/cm^2 by means of a Phenix 3000 type
exposing machine manufactured by ORC Factory Co., Ltd.
by using a negative mask for test shown in Figure 2. In
Figure 2, 3 shows an opaque part of the negative mask
and 4 shows a transparent part of the negative mask,
15 and the unit of the figures is mm. After the exposure,
the test substrates were allowed to stand for 30 minutes,
and then subjected to spray development at 20°C for 90
seconds by using 1,1,1-trichloroethane.

After the development, the test substrates
20 were heated and dried at 80°C for 10 minutes, and then
irradiated at 2.5 J/cm^2 by using an ultraviolet light
irradiating equipment manufactured by Toshiba Denzai
Co., Ltd.

Thereafter, they were heat-treated at 150°C
25 for 30 minutes. Four of the six test substrates on
which a protective coating film was thus formed were
immersed in isopropanol, toluene, trichlene, or a 10%
aqueous hydrochloric acid solution all at 25°C , respectively,

- 1 for 10 minutes to find that the formed protective coating film underwent no change.

When another one of the test substrates was immersed in a soldering bath at 255° to 265°C for 30
5 seconds, its protective coating film was so stable that it did neither crack nor peel off from the substrate, and therefore it was found to be sufficiently usable as a soldering mask.

Further, the remaining one test substrate was
10 subjected to soldering treatment in a soldering bath at 255° to 265°C for 3 seconds by using a rosin series flux A-226 (manufactured by Tamura Kaken Co., Ltd.), and then subjected to the thermal shock test of 20 cycles under MIL-STD-202E method 107D condition B (-65°C for 30 minutes
15 ± ordinary temperature for 5 minutes or less ± 125°C for 30 minutes). As a result, its protective coating film did not crack and was found to be greatly excellent in long-term reliability.

Example 10

a) Synthesis of a urethane diacrylate compound

A. Isophorone diisocyanate	1,776 parts (16 equivalents)
Toluene (solvent)	800 parts
Di-n-butyl tin dilaurate (catalyst)	1 part

B	1,4-Cyclohexane dimethanol	360 parts (5 equivalents)
	2-Hydroxyethyl acrylate	348 parts (3 equivalents)
	Methyl ethyl ketone (solvent)	520 parts
C	2-Hydroxyethyl acrylate	928 parts (8 equivalents)
	Toluene (solvent)	80 parts
	p-Methoxyphenol (thermopolymerization inhibitor)	0.3 part
D	Ethanol (stopping agent)	23 parts

1 A solution of a urethane diacrylate compound was obtained according to the above recipe in the same manner as in Example 9-a). Thereafter, it was dried under reduced pressure to obtain a viscous urethane

5 diacrylate compound (IX).

b) Production of a photosensitive element

The urethane diacrylate compound (IX) obtained in the manner described above	40 parts
Methyl methacrylate-methyl acrylate-2-hydroxyethyl methacrylate-acrylonitrile (80/10/5/5 weight ratio) copolymer (having a	57 parts

molecular weight of about 100,000 and a glass transition temperature of about 90°C)

Benzophenone	2.7 parts
Michler's ketone	0.3 part
p-Methoxyphenol	0.1 part
Victoria pure blue	0.05 part
Methyl ethyl ketone	80 parts
Toluene	40 parts

1 A solution 10 of a photosensitive resin composition prepared from the above recipe was uniformly applied to a polyethylene terephthalate film 16 of 25 μ m in thickness by using an apparatus shown in Figure 3, and
5 then dried in a hot-air convention dryer 11 at 80° to 100°C for about 10 minutes. The thickness after drying of the layer of the photosensitive resin composition was about 100 μ m. A polyethylene film 17 of about 25 μ m in thickness was stuck, as a covering film, on the layer
10 of the photosensitive resin composition, as shown in Figure 3. In Figure 3, 5 shows a polyethylene terephthalate film delivering roll, 6, 7 and 8 rolls, 9 a knife, 12 a polyethylene film delivering roll, 13 and 14 rolls and 15 a photosensitive element wiring roll.

15 c) Formation of a soldering mask

The photosensitive element obtained in the above was laminated with heating under pressure on a printed wiring board for test (having a glass epoxy

1 substrate and a thickness of 1.6 mm) in which a copper
pattern (copper thickness: about 70 μm) shown in Figure 1
had been formed, by using a vacuum laminater manufactured
by Hitachi Chemical Industry Co., Ltd. (degree of
5 vacuum: 30 mmHg, lamination temperature: 100°C, lamination
speed: 2 m/min.). After the lamination, the printed wiring
boards were heated at 60°C for 5 minutes, allowed to
stand at room temperature for 3 hours, and then exposed
at 150 mJ/cm^2 through a negative mask for test shown
10 in Figure 2, as in Example 9-c).

After the exposure, the boards were heated
at 80°C for 5 minutes and then allowed to stand at room
temperature for 20 minutes, after which the support film
was peeled off, and the boards were subjected to spray
15 development at 20°C for 150 seconds by using 1,1,1-
trichloroethane.

After the development, the boards were heated
and dried at 80°C for 10 minutes, irradiated with ultra-
violet light at 3.0 J/cm^2 , and then heat-treated at 130°C
20 for 2 hours.

The test substrates on which a protecting
coating film had been formed in the manner described
above were subjected to the immersion test for 10 minutes
in isopropanol, toluene, trichlene, or a 10% aqueous
25 hydrochloric acid solution all at 25°C in the same manner
as in Example 9-c) to find that the formed protective
coating film underwent no change.

When the immersion test was carried out in a

- 1 soldering bath at 255° to 265°C for 30 seconds, the protective coating film showed no defect and hence was excellent in heat resistance. After the same soldering treatment as in Example 9-c), the formed coating film
- 5 did not crack in the thermal shock test of 20 cycles under MIL-STD-202E method 107D condition B.

Example 11

The urethane diacrylate compound (IX) obtained in Example 10-a)	60 parts
Methyl methacrylate-methacrylic acid (98/2 weight ratio) copolymer (having a molecular weight of about 100,000 and a glass transition temperature of about 105°C)	37 parts
Benzophenone	2.7 parts
Michler's ketone	0.3 part
p-Methoxyphenol	0.1 part
Victoria pure blue	0.02 part
Methyl ethyl ketone	60 parts
Toluene	70 parts

By the use of a solution of a photosensitive resin composition prepared from the above recipe, a photosensitive element in which the thickness of a layer of the photosensitive resin composition was about 80 μ m was obtained by using an apparatus shown in Figure 3, as in Example 10-b). The photosensitive element was laminated under reduced pressure in the same manner as

15 in Example 10-c) on printed wiring boards for test on

1 which a copper pattern (copper thickness: about 50 μ m)
shown in Figure 1 had been formed. Further, the same
treatment as in Example 10-c) was carried out to form
an imagewise protective coating film on said test
5 substrates. The formed protective coating film showed
no defect in the immersion test for 10 minutes in
isopropanol, toluene, trichlene, methyl ethyl ketone,
a 10% aqueous hydrochloric acid solution or a 10% aqueous
NaOH solution all at 25°C, and was so excellent in heat
10 resistance that it did neither crack nor peel off from
the substrate in the immersion test for 30 seconds in
a soldering bath at 255° to 265°C after the same solder-
ing treatment as in Example 9-c). After the same soldering
treatment as in Example 9-c), the protective coating
15 film did not crack in the thermal shock test of 20 cycles
under MIL-STD-202E method 107D condition B.

Comparative Example 5

The same procedures as in Example 10-b) and
Example 10-c) were followed, with the exception that
20 trimethylolpropane triacrylate was substituted for the
urethane diacrylate compound (IX) in Example 10-b). The
finally obtained protective coating film partly peeled
off from the substrate in the immersion test for 30 seconds
in a soldering bath at 255° to 265°C. After the same
25 soldering treatment as in Example 9-c), the protective
coating film cracked within 5 cycles in the thermal
shock test under MIL-STD-202E method 107D condition B.

1 Comparative Example 6

The same procedure as in Example 11 was followed, with the exception that 20 parts of pentaerythritol triacrylate and 40 parts of di-(3-acryloxy-2-hydroxy-
5 propyl) ester of bisphenol A were substituted for 60 parts of the urethane diacrylate compound (IX) in Example 11. The finally obtained protective coating film cracked in the thermal shock test of 5 cycles under MIL-STD-202E method 107D condition B after the same soldering treatment
10 as in Example 9-c). A part of the protective coating film was about to peel off from the substrate in the immersion test for 10 minutes in a 10% aqueous hydrochloric acid solution.

Comparative Example 7

Trimethylolpropane triacrylate	30 parts
Polypropylene glycol (having an average molecular weight of 1,000) diacrylate	10 parts
Methyl methacrylate-methacrylic acid-tetrahydrofurfuryl methacrylate (78/2/20 weight ratio) copolymer (having a molecular weight of about 150,000 and a glass transition temperature of about 95°C)	50 parts
Benzophenone	2.7 parts
Michler's ketone	0.3 part
p-Methoxyphenol	0.5 part
Methyl ethyl ketone	200 parts

The same procedure as in Example 11 was followed,

- 1 with the exception that a solution of a photosensitive resin composition prepared from the above recipe was used. The finally obtained protective coating film was excellent in solvent resistance and heat resistance,
- 5 but cracked within 10 cycles in the thermal shock test under MIL-STD-202E method 107D condition B after the same soldering treatment as in Example 9-c).

Example 12

a) Synthesis of a urethane diacrylate compound

A	Isophorone diisocyanate	1,776 parts (16 equivalents)
	Toluene (solvent)	1,200 parts
	Di-n-butyl tin dilaurate (catalyst)	1 part
B	Tetraethylene glycol	776 parts (8 equivalents)
C	2-Hydroxypropyl acrylate	1,040 parts (8 equivalents)
	Toluene (solvent)	300 parts
	Hydroquinone (thermopolymerization inhibitor)	0.4 part
D	Methanol (stopping agent)	32 parts

A solution of a urethane diacrylate compound

10 was obtained according to the above recipe in the same manner as in Example 9-a). Thereafter, it was dried under reduced pressure to obtain a viscous urethane diacrylate compound (X).

1 b) Production of a photosensitive element and formation of a soldering mask

The urethane diacrylate compound (X) obtained in the manner described above	60 parts
Methyl methacrylate-methacrylic acid-tribromophenyl acrylate (38/2/60 weight ratio) copolymer (having a molecular weight of about 120,000, a glass transition temperature of about 120°C and a bromine content of 37% by weight)	37 parts
Benzophenone	2.7 parts
4,4'-Bis(diethylamino)benzophenone	0.3 part
2,2'-Methylenebis(4-ethyl-6-t-butylphenol)	0.3 part
Victoria pure blue	0.02 part
Methyl ethyl ketone	100 parts
Toluene	50 parts

 The same procedures as in Example 10-b) and Example 10-c) were followed, with the exception that

5 a solution of a photosensitive resin composition prepared from the above recipe was used. The finally obtained protective coating film showed no defect in the immersion test for 10 minutes in isopropanol, toluene, trichlene or a 10% aqueous hydrochloric acid solution

10 all at 25°C, and underwent no change such as peeling-off and cracking when immersed in a soldering bath at 255° to 265°C for 30 seconds. It did not crack also in the thermal shock test of 20 cycles under MIL-STD-202E method 107D condition B after the same soldering treatment as

15 in Example 9-c). A protective coating film was formed

- 1 of the same procedure as in the above on the whole surface of a substrate of 0.8 mm in thickness of a printed wiring substrate MCL-E-68 (UL flame-retardancy grade 94V-0) manufactured by Hitachi Chemical Co., Ltd.
- 5 This coating film satisfied the standards of 94V-1 of UL.

Example 13

a) Synthesis of a urethane diacrylate compound

A	Isophorone diisocyanate	1,776 parts (16 equivalents)
	Toluene (solvent)	1,000 parts
	Di-n-butyl tin dilaurate (catalyst)	1 part
B	Ethylene glycol	310 parts (10 equivalents)
C	2-Hydroxyethyl acrylate	696 parts (6 equivalents)
	Toluene (solvent)	150 parts
	Hydroquinone (thermopolymerization inhibitor)	0.3 part
D	Methanol (stopping agent)	32 parts

- A solution of a urethane diacrylate compound
- 10 was obtained according to the above recipe in the same manner as in Example 10-a). Thereafter, it was dried under reduced pressure to obtain a viscous urethane diacrylate compound (XI).

1 b) Production of a photosensitive element and formation of a soldering mask

The urethane diacrylate compound (XI) obtained in the manner described above	50 parts
Methyl methacrylate-methyl acrylate-acrylic acid-tetrahydrofurfuryl methacrylate-tribromophenyl acrylate (40/23/2/10/25 weight ratio) copolymer (having a molecular weight of about 80,000, a glass transition temperature of about 75°C and a bromine content of 15%)	47 parts
Benzophenone	2.7 parts
Michler's ketone	0.3 part
2,2'-Methylenebis(4-methyl-6-t-butylphenol)	0.5 part
Victoria pure blue	0.02 part
Methyl ethyl ketone	100 parts
Toluene	50 parts

The same procedures as in Example 10-b) and Example 10-c) were followed, with the exception that

5 a solution of a photosensitive resin composition prepared from the above recipe was used. The finally obtained protective coating film showed no defect in the immersion test for 10 minutes in isopropanol, toluene, trichlene or a 10% aqueous hydrochloric acid solution all at 25°C,

10 and underwent no change such as peeling-off and cracking when immersed in a soldering bath at 255° to 265°C for 30 seconds. It did not crack also in the thermal shock test of 20 cycles under MIL-STD-202E method 107D condition B after the same soldering treatment as in Example

- 1 9-c). A protective coating film was formed by the same
procedure as in the above on the whole surface of a
substrate of 1.6 mm in thickness of a printed wiring
substrate MCL-E-68 manufactured by Hitachi Chemical
5 Co., Ltd. This coating film satisfied the standards of
94V-1 of UL.

Example 14

The same procedure as in Example 13 was followed,
with the exception that 1 part of antimony trioxide was
10 additionally incorporated into the solution of a photo-
sensitive resin composition in Example 13-b). The
finally obtained protective coating film was as good as
in Example 13-b) in solvent resistance, heat resistance
and resistance to thermal shock. A protective coating
15 film was formed by the same procedure as in the above
on the whole surface of a substrate of 1.6 mm in thickness
of a printed wiring substrate MCL-E-68 manufactured by
Hitachi Chemical Co., Ltd. This coating film satisfied
the standards of 94V-0 of UL.

Example 15

a) Synthesis of a urethane dimethacrylate compound

A Isophorone diisocyanate	1,776 parts (16 equivalents)
Toluene (solvent)	1,000 parts
Di-n-butyl tin dilaurate (catalyst)	1 part

(21)

B	1,4-Butanediol	360 parts (8 equivalents)
C	2-Hydroxyethyl methacrylate	1,040 parts (8 equivalents)
	Toluene (solvent)	280 parts
	Hydroquinone (thermopolymerization inhibitor)	0.3 part
D	Methanol (stopping agent)	32 parts

1. A solution of a urethane diacrylate compound was obtained according to the above recipe in the same manner as in Example 9-a). Thereafter, it was dried under reduced pressure to obtain a viscous urethane dimethacrylate compound (XII).

b) Production of a photosensitive element and formation of a soldering mask

The urethane dimethacrylate compound (XII) obtained in the manner described above	40 parts
Methyl methacrylate-methacrylic acid-tetrahydrofurfuryl methacrylate-acrylonitrile-tribromophenyl acrylate (43/2/20/5/30 weight ratio) copolymer (having a molecular weight of 150,000, a glass transition temperature of about 100°C and a bromine content of 18% by weight)	57 parts
Benzophenone	2.7 parts
Michler's ketone	0.3 part
p-Methoxyphenol	0.05 part
Victoria pure blue	0.05 part
Toluene	150 parts

1 The same procedures as in Example 10-b) and
Example 10-c) were followed, with the exception that a
solution of a photosensitive resin composition prepared
from the above recipe was used. The finally obtained
5 protective coating film showed no defect in the immersion
test for 10 minutes in isopropanol, toluene, trichlene
or a 10% aqueous hydrochloric acid solution all at 25°C,
and underwent no change such as peeling off and cracking
when immersed in a soldering bath at 255° to 265°C for 30
10 seconds. Further, it did not crack also in the thermal
shock test of 20 cycles under MIL-STD-202E method 107D
condition B after the same soldering treatment as in
Example 9-c). A protective coating film was formed by
the same procedure as in the above on the whole surface
15 of a substrate of 1.6 mm in thickness of a printed wiring
substrate MCL-E-68 manufactured by Hitachi Chemical
Co., Ltd. This coating film satisfied the standards of
94V-1 of UL.

Example 16

- 20 a) Synthesis of a urethane diacrylate compound
- | | | |
|---|--|---------------------------------|
| A | Isophorone diisocyanate | 1,776 parts
(16 equivalents) |
| | Toluene (solvent) | 1,000 parts |
| | Di-n-butyl tin dilaurate
(catalyst) | 1 part |
| B | 1,4-Cyclohexanedi-
methanol | 216 parts
(3 equivalents) |
| | Tetraethylene glycol | 291 parts
(3 equivalents) |

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	Methyl ethyl ketone (solvent)	200 parts
C	2-Hydroxyethyl	1,160 parts (10 equivalents)
	Toluene (solvent)	200 parts
	p-Methoxyphenol (thermopolymerization inhibitor)	0.2 part
D	Methanol	32 parts

1 A solution of a urethane diacrylate compound was
obtained according to the above recipe in the same manner
as in Example 9-a). Thereafter, it was dried under
reduced pressure to obtain a viscous urethane diacrylate
5 compound (XIII).

b) Production of a photosensitive element

The urethane diacrylate compound (XIII) obtained in the manner described above	47 parts
Methyl methacrylate-methyl acrylate- acrylic acid-tetrahydrofurfuryl methacrylate-2-hydroxyethyl methacrylate-tribromophenyl acrylate (43/10/2/5/5/35 weight ratio) copolymer (having a molecular weight of about 150,000, a glass transition temperature of about 90°C and a bromine content of 22% by weight)	50 parts
Benzophenone	2.7 parts
Michler's ketone	0.3 part
p-Methoxyphenol	0.05 part
Victoria pure blue	0.02 part

KAYAMER PA-2 (manufactured by Nihon Kayaku Co., Ltd., a divalent acrylate containing a phosphoric acid group)	0.1 part
Methyl ethyl ketone	50 parts
Toluene	100 parts

1 By the use of a solution of a photosensitive
resin composition prepared from the above recipe, a photo-
sensitive element in which the thickness of a layer of
the photosensitive resin composition was about 50 μm
5 was obtained by using, as in Example 10-b), an apparatus
shown in Figure 3.

c) Formation of a soldering mask

The photosensitive element obtained in the above
was laminated, under reduced pressure in the same manner
10 as in Example 10-c), on a printed wiring board for test
on which a copper pattern (copper thickness: about 18 μm)
shown in Figure 1 had been formed. After the lamination,
the printed wiring boards were allowed to stand at room
temperature for 3 hours, and then exposed, as in
15 Example 9-c), at 200 mJ/cm^2 through a negative mask for
test shown in Figure 2. After the exposure, the boards
were heated at 80°C for 5 minutes and then allowed to
cool at room temperature for 20 minutes, after which
the support film was peeled off, and the boards were
20 subjected to spray development at 20°C for 70 seconds
by using 1,1,1-trichloroethane. After the development,

1 the boards were heated and dried at 80°C for 30 minutes,
and further heated at 120°C for 30 minutes and then at
150°C for 30 minutes. The heated boards were allowed to
cool at room temperature for 10 minutes, irradiated
5 with ultraviolet light at 10 J/cm², and then heat-treated
at 130°C for 2 hours. The test substrates on which
a protective coating film was thus formed were subjected
to the immersion test for 10 minutes in isopropanol, toluene,
trichlene or a 10% aqueous hydrochloric acid solution all
10 at 25°C in the same manner as in Example 9-c) to find that
the protective coating film showed no defect. The
protective coating film did not peel off in the immersion
test for 30 seconds in a soldering bath at 255° to 265°C,
and hence was good in heat resistance. Further, it did
15 not crack in the thermal shock test of 20 cycles under
MIL-STD-202E method 107D condition B after the same solder-
ing treatment as in Example 9-c). The protective coating
film did not peel off in the cross-cutting test, and
hence is excellent in adhesion. A protective coating
20 film was formed by the same procedure as in the above
on the whole surface of a substrate of 0.8 mm in thick-
ness of a printed wiring substrate MCL-E-68 manufactured
by Hitachi Chemical Co., Ltd. This coating film satisfied
the standards of 94V-1 of UL.

25 Comparative Example 8

A urethane diacrylate compound was synthesized
in the same manner as in Example 9-a), except that

1 1,344 parts (16 equivalents) of hexamethylene diisocyanate
was substituted for 1,776 parts (16 equivalents) of
the isophorone diisocyanate. The produced urethane
diacrylate compound (XIV) was insoluble in toluene, the
5 reaction solvent, and separated as wax just as it was
produced. The obtained urethane diacrylate compound
(XIV) was slightly soluble in methyl ethyl ketone and
1,1,1-trichloroethane, and soluble in acetone and
chloroform.

The urethane diacrylate compound (XIV) obtained in the above	50 parts
The copolymer used in Example 9-b)	47 parts
Benzophenone	2.7 parts
Michler's ketone	0.3 part
p-Methoxyphenol	0.05 part
Victoria pure blue	0.02 part
Acetone	50 parts
Chloroform	100 parts

10 A solution of a photosensitive resin com-
position prepared from the above recipe was applied to
a polyethylene terephthalate film by using, as in
Example 10-b), an apparatus shown in Figure 3, and then
dried in hot air to find that the urethane diacrylate
15 compound (XIV) and the copolymer separated from each
other just as the solvent was dried, so that no desirable
photosensitive element could be obtained. When any
of the copolymers used in Examples 10 to 16 was used,

1. the miscibility was as low as in the above, and no desirable photosensitive element could be obtained.

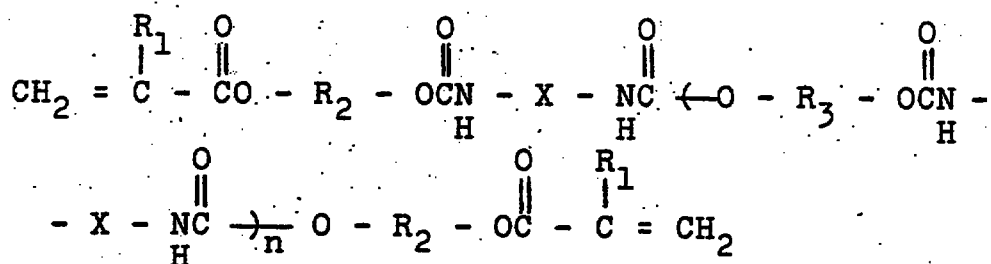
As explained in detail in Examples, the photosensitive resin composition and the photosensitive

5. element of this invention give a protective coating film excellent in heat resistance, resistance to thermal shock and solvent resistance, and the given protective coating film is suitable as a soldering mask which is required to have long-term reliability.

C L A I M S



1. A photosensitive resin composition comprising
 - (a) 20 to 75 parts by weight of a urethane diacrylate or urethane dimethacrylate compound obtained by reacting,
 - (i) trimethylhexamethylene diisocyanate and/or isophorone diisocyanate,
 - (ii) a dihydric alcohol, and
 - (iii) an acrylic or methacrylic monoester of a dihydric alcohol,
 - (b) 20 to 75 parts by weight of a linear polymeric compound having a glass transition temperature of about 40° to 150°C, and
 - (c) a sensitizer and/or a sensitizer system which generate free radicals when exposed to actinic light
2. A composition according to Claim 1, wherein the diisocyanate (i) is trimethylhexamethylene diisocyanate.
3. A composition according to Claim 1, wherein the diisocyanate (i) is isophorone diisocyanate.
4. A composition according to Claim 1, wherein the urethane diacrylate or dimethacrylate compound (a) is represented by the following formula:



wherein R_1 is H or CH_3 ; R_2 is a residue of a dihydric alcohol; R_3 is a residue of a dihydric alcohol; X is a residue of isophorone diisocyanate or a trimethylhexamethylene group; and n is zero or a positive integer.

5. A composition according to any one of the preceding claims wherein the dihydric alcohol (ii) and (iii) have 1 to 23 carbon atoms.

6. A composition according to any one of the preceding claims wherein the dihydric alcohol (ii) is 1,4-butanediol, 1,3-butanediol, 1,5-pentanediol, 1,6-hexanediol or 1,4-cyclohexanedimethanol.

7. A composition according to any one of the preceding claims wherein the acrylic or methacrylic monoester (iii) of a dihydric alcohol is hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate or hydroxypropyl methacrylate.

8. A composition according to any one of the preceding claims wherein the urethane diacrylate or dimethacrylate compound (a) contains acryloyl or methacryloyl groups in an amount of 1×10^{-3} to 4.3×10^{-3} equivalent/g.

9. A composition according to any one of the preceding claims wherein the linear polymeric compound (b) is a vinyl series copolymer.



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10. A composition according to any one of the preceding claims wherein the linear polymeric compound (b) contains bromine atoms in an amount up to 40% by weight.
11. A composition according to any one of the preceding claims wherein the linear polymeric compound (b) contains 5 to 65% by weight of tribromophenyl acrylate or tribromophenyl methacrylate as a copolymer component.
12. A composition according to any one of the preceding claims which additionally contains an acrylic or methacrylic ester containing a phosphoric acid group in the molecule.
13. A composition according to any one of the preceding claims which additionally contains antimony trioxide in an amount up to 5% by weight.
14. A composition according to claim 1 substantially as hereinbefore described with reference to any one of the Examples.
15. A photosensitive element comprising (I) a layer of a photosensitive resin composition according to any one of the preceding claims and (II) a support film supporting said layer.
16. A photosensitive element according to claim 15, wherein the layer (I) of the photosensitive resin composition has a thickness of 20 to 200 μm .
17. A photosensitive element according to claim 15 or 16, wherein the support film (II) is a polyester film, a polyimide film, a polyamide-imide film, a polypropylene film or a polystyrene film.



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18. A photosensitive element according to any one of claims 15 - 17 which further laminates a releasable covering film on the layer (I) of the photosensitive resin composition.

19. A photosensitive element according to claim 15 substantially as hereinbefore described with reference to any one of the Examples.

20. A soldering mask comprising a photosensitive element according to any one of claims 15 -19.

21. A process for the preparation of a photosensitive resin composition as defined in any one of claims 1 - 14 substantially as hereinbefore described with reference to any one of the Examples.

22. A process for the preparation of a photosensitive element as defined in any one of claim 15-19 substantially as hereinbefore described with reference to any one of the Examples.

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