

**"PHOTOSENSITIVE RESIN COMPOSITION AND  
PHOTOSENSITIVE ELEMENT USING THE SAME"**

1           This invention relates to a photosensitive  
resin composition and a photosensitive element using  
such a composition. More particularly, it relates to  
a photosensitive resin composition improved in adhesive-  
5   ness and usable for soldering masks (permanent protec-  
tive masks), etc., such as used in production of printed  
wiring boards, and to a photosensitive element using  
such a composition.

          It is well known that photosensitive resin  
10   compositions are used as photoresist in production of  
printed wiring boards. It is also known that photo-  
sensitive elements comprising a support film and a layer  
of a substantially dried photosensitive resin composi-  
tion laminated thereon can be used as photoresist in  
15   producing printed wiring boards.

          Photosensitive resin compositions or photo-  
sensitive elements used for producing printed wiring  
boards may be roughly divided into the following two  
types according to the purposes of use. One is the type  
20   used for forming a wiring pattern which forms a resist  
image in etching or metal plating and the other is the  
type used for forming a soldering mask.

          Either of these types is required to have  
adhesiveness to the substrate employed, but the  
25   significance of such adhesiveness differs greatly

1 from one type to the other. That is, adhesiveness  
required in the former type is such as to merely inhibit  
penetration of the etching or plating solution of a  
temperature ranging from room temperature to 100°C  
5 at highest only during the etching or plating operation  
while allowing easy and perfect separation of the resist  
from the substrate after the etching or plating treatment.  
In other words, adhesiveness required in this type is  
of merely temporary nature.

10 On the other hand, adhesiveness in the latter  
type means permanent one and it is required to be strong  
enough to prevent penetrating of the solder or floating  
of the mask during immersion in a soldering bath of  
a high temperature (usually 240° to 300°C).

15 Concerning the former type, there is proposed  
in U.S. Patent No. 3,622,334 improvement of etching and  
plating resistance by addition of benzimidazole, 2-  
aminobenzothiazole, benzotriazole or derivatives thereof.

However, the effect of such additives in the  
20 case of the latter type is not known, and the results of  
the experiments conducted by the present inventors showed  
total ineffectiveness of said additives for the latter  
type of the photosensitive resin compositions. This is  
considered due to the fact that adhesiveness required  
25 in the latter type is of different nature from plating  
resistance, etc., and is quite "strict" one as mentioned  
before.

U.S. Patent No. 4,272,607 discloses phosphorus-

4 1 containing acrylic acid derivatives as examples of the  
photopolymerizable unsaturated compounds constituting  
the photosensitive resin compositions, but there is  
given no suggestion as to the effect thereof on soldering  
5 heat resistance, and also the experiments by the present  
inventors clarified that almost no effect is produced  
by single use of such compounds.

As a result of extensive studies on these  
photosensitive resin compositions, the present inventors  
10 found that soldering heat resistance is surprisingly  
improved when a phosphate compound having photopolymeriz-  
able unsaturated bonds is used in combination with  
such a substance as benzotriazole, benzimidazole,  
benzothiazole, etc., and the present invention was  
15 attained on the basis of such finding.

An object of this invention is to provide a  
photosensitive resin composition improved in adhesiveness  
to the substrate and usable for forming soldering masks,  
etc., and a photosensitive element using such a composi-  
20 tion.

Thus, the present invention provides a photo-  
sensitive resin composition comprising:

- (a) at least one compound selected from the group  
consisting of benzotriazole, benzimidazole, benzothiazole,  
25 derivatives thereof and salts thereof,
- (b) a phosphate compound having at least one  
photopolymerizable unsaturated bond,
- (c) if necessary, an organic thermoplastic polymer,

- 1 (d) a photopolymerizable unsaturated compound  
having at least one terminal ethylene group, and  
(e) a sensitizer and/or a sensitizer system capable  
of initiating polymerization of said unsaturated com-  
5 pounds (b) and (d) upon irradiation of actinic light.

The present invention also provides a photo-  
sensitive element comprising a layer of a photosensitive  
resin composition and a support film therefor, said  
photosensitive resin composition containing (a) at least  
10 one compound selected from the group consisting of  
benzotriazole, benzimidazole, benzothiazole, derivatives  
thereof and salts thereof, (b) a phosphate compound  
having at least one photopolymerizable unsaturated bond (c) an  
organic thermoplastic polymer, (d) a photopolymerizable  
15 compound having at least one terminal ethylene group, and (e)  
a sensitizer and/or a sensitizer system capable of  
initiating polymerization of said unsaturated compounds  
(b) and (d) upon irradiation of actinic light.

In the accompanying drawings, Figs. 1 and 2  
20 are sectional views showing examples of the photosensitive  
elements according to this invention; Fig. 3 is a  
schematic drawing of an apparatus for producing the  
photosensitive elements used in the Examples described  
later; Fig. 4 is a drawing showing a negative mask for  
25 testing used in the Examples; and Fig. 5 is a drawing  
showing a copper pattern on the test substrate used  
in the Examples.

The photosensitive resin composition and

(P)

- 1 the photosensitive element according to the present invention are described in detail hereinbelow.

Description is first made on the respective components of the photosensitive resin composition of this invention. As the component (a) of the composition, there is selected at least one compound chosen from the group consisting of benzotriazole, benzimidazole, benzothiazole, derivatives thereof and salts thereof. The term "derivatives thereof" as used herein means 10 these compounds in which a hydrogen atom or atoms are substituted with at least one alkyl group, aryl group, nitro group, halogen, amino group, hydroxyl group or carboxyl group or those in which the benzene ring has been replaced by a naphthalene ring. The 15 term "salts thereof" means acid salts, such as hydrochlorides, acetates, etc., of said compounds, amine salts, etc.

Preferred examples of these compounds are benzotriazole, benzotriazole hydrochloride, 1-chloro- 20 benzotriazole, hydroxybenzotriazole, naphthotriazole, methylbenzotriazole and amine salts, etc., thereof; benzimidazole, benzimidazole hydrochloride, 2-amino-benzimidazole, 2-methylbenzimidazole, 5-nitrobenzimidazole, 5-methylbenzimidazole, etc.; and 2-aminobenzothiazole, 25 2-aminobenzothiazole hydrochloride, etc. Among these salts, hydrochlorides are preferred because of their easiness of preparation. A noticeable effect of addition of these compounds can be obtained from the compound

1 content of about 0.001% by weight or more in the photo-  
sensitive resin composition, but preferably said compound  
is added in an amount of 0.01 to 3% by weight in the  
photosensitive resin composition.

5 Preferred examples of the phosphate compounds  
having photopolymerizable unsaturated bonds used as  
component (b) of the composition include PHOSMER-M  
(a trade name of an acid phosphoxyethyl methacrylate,  
manufactured by Yushi Seihin Co., Ltd.), PHOSMER-CL  
10 (3-chloro-2-acid phosphoxypropyl methacrylate), PM-2  
(bis(methacryloxyethyl)phosphate), PA-1 (acryloxyethyl  
phosphate) and PA-2 (bis(acryloxyethyl) phosphate) in  
KAYAMER<sup>®</sup> series manufactured by Nippon Kayaku Co., Ltd.,  
and VINYATE-R (bis(2-chloro-ethyl)-vinyl phosphate)  
15 and PS-A4 (1,2-bis(carboxyallyl)-ethyl-dibutyl phosphate)  
manufactured by Daihachi Chemical Industry. These com-  
pounds exhibit their effect when they are added in an  
amount of about 0.001% by weight or more in the photo-  
sensitive resin composition, but it is usually preferred  
20 to use such compounds in an amount of 0.01 to 10% by  
weight in the composition.

The component (c), or an organic thermoplastic  
polymer, is added at need, but in case of forming a  
photosensitive element, such polymer is an essential  
25 component for giving the film properties to the resin  
composition. Employable as such organic thermoplastic  
polymer are those disclosed in U.S. Patent No. 3,261,686.  
For example, there may be used polyamides such as alcohol-

1 soluble nylon, vinyl polymers such as poly(methyl meth-  
acrylate), vinyl copolymers such as methyl methacrylate/  
acrylic acid/styrene copolymer, celluloses such as  
cellulose acetate, and polyesters such as butanediol/  
5 isophthalic acid/sebacic acid condensation polymer.  
Among them, linear vinyl copolymers are preferred  
because of their compatibility with other components  
and good adhesiveness to the substrate surface. Various  
types of vinyl monomers may be used as the copolymeriza-  
10 tion component of these polymers. As typical examples  
of such vinyl monomers, there may be cited methyl  
methacrylate, butyl methacrylate, ethyl acrylate, styrene,  
 $\alpha$ -methylstyrene, vinyltoluene, 2-hydroxyethyl meth-  
acrylate, 2-hydroxypropyl acrylate, acrylic acid, meth-  
15 acrylic acid, glycidyl methacrylate, t-butylaminoethyl  
methacrylate, 2,3-dibromopropyl methacrylate, 3-chloro-  
2-hydroxypropyl methacrylate, tetrahydrofurfuryl meth-  
acrylate, tribromophenyl acrylate, acrylamide, acrylo-  
nitrile, butadiene, etc. The content of such organic  
20 thermoplastic polymer in the photosensitive resin compo-  
sition is preferably in the range of 20 to 80 parts by  
weight for the reason of maintaining the film properties  
and photosetting property of the composition.

Used as the component (d) of the photosensitive  
25 resin composition of this invention is a photopolymeriz-  
able unsaturated compound having at least one terminal  
ethyl group. As examples of such compounds, there may  
be cited the photopolymerizable compounds disclosed in

1 Japanese Patent Appln Kokeku (Post-Exam Publn) No. 37214/78,  
the monomers disclosed in U.S. Patent No. 3,632,636, and  
photopolymerizable urethane di(meth)acrylate (i.e., diacryl-  
ate or dimethacrylate) compounds. Typical examples of the  
5 photopolymerizable unsaturated compounds usable in this  
invention are trimethylolpropane triacrylate, trimethylol-  
propane trimethacrylate, pentaerythritol triacrylate,  
ethylene glycol diacrylate, diethylene glycol diacrylate,  
2,2-di(p-hydroxyphenyl)-propane diacrylate, di-(3-acryloxy-  
10 2-hydroxypropyl) ester of tetrabromobisphenol A, etc.

The urethane di(meth)acrylate compounds can be  
obtained by reacting (i) at least one diisocyanate compound  
selected from isophorone diisocyanate and trimethyl-  
hexamethylene diisocyanate, (ii) optionally a dihydric alcohol  
15 and (iii) a (meth)acrylic (i.e., acrylic or methacrylic)  
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 tri-  
20 methylhexamethylene 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  
25 (iii), there can be used ethylene glycol, diethylene  
glycol, triethylene glycol, tetraethylene glycol, pro-  
pylene glycol, dipropylene glycol, 1,4-butanediol, 1,3-  
butanediol, 2,3-butanediol, 1,5-pentanediol, 1,6-hexanediol,

5 As the (meth)acrylic monoester of a dihydric alcohol, there can be used 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 1,4-butanediol mono(meth)-acrylate, 1,3-butanediol mono(meth)acrylate, and the like.

$$\text{CH}_2 = \overset{\text{R}_1}{\underset{|}{\text{C}}} - \overset{\text{O}}{\parallel} \text{CO} - \text{R}_2 - \overset{\text{O}}{\parallel} \text{OCN} - \underset{\text{H}}{\text{X}} - \underset{\text{H}}{\text{NC}} = \text{O} - \text{O} - \text{R}_3 - \overset{\text{O}}{\parallel} \text{OCN} - \underset{\text{H}}{\text{H}}$$

In the formula (I),  $R_1$  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 an integer preferably from 1 to 3. The actually obtained reaction product is a mixture of urethane di(meth)acrylate compounds in which the values of n are different.

1           When the urethane di(meth)acrylate compound  
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),  
5 the dihydric alcohol (ii) and the (meth)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 alcohol (ii) and the (meth)-  
10 acrylic monoester of a dihydric 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 are finally reacted with a  
15 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  
equivalent of the (meth)acrylic monoester of a dihydric  
20 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.

These compounds were cited merely by way of  
25 exemplification and not in a restrictive sense. The  
content of such photopolymerizable unsaturated compound  
having at least one terminal ethylene group in the photo-  
sensitive resin composition of this invention is

- 1 preferably within the range of 20 to 80 parts by weight for the reason of film properties and photosetting properties.

Used as component (e) of the photosensitive  
5 resin composition of this invention is a sensitizer and/or a sensitizer system which initiates polymerization of said unsaturated compounds (b) and (d) upon irradiation of actinic light. Examples of the sensitizers usable in this invention are substituted or unsubstituted poly-  
10 nuclear quinones such as 2-ethylanthraquinone, 2-t-butylanthraquinone, octamethylanthraquinone, 1,2-benzanthraquinone, 2,3-diphenylanthraquinone, etc.; ketoaldonyl compounds such as diacetyl, benzyl, etc.;  $\alpha$ -ketoaldonyl alcohols and ethers such as benzoin, pivalone,  
15 etc.;  $\alpha$ -hydrocarbon-substituted aromatic acyloins such as  $\alpha$ -phenyl-benzoin,  $\alpha,\alpha$ -diethoxyacetophenone, etc.; and aromatic ketones such as benzophenone, 4,4'-bisdialkylaminobenzophenone, etc. These sensitizers may be used either singly or in combination.

20 The term "sensitizer system" is used herein to mean a combination of a sensitizer and a sensitizing assistant. Examples of such sensitizer system are combinations of 2,4,5-triarylimidazole dimer and 2-mercaptobenzoquinazole, leucocrystal violet, tris(4-  
25 diethylamino-2-methylphenyl)methane and the like. It is possible to use such type of additives which, although having no photoinitiating property per se, can provide a sensitizer system with even better photoinitiating

1 performance as a whole when used in combination with  
above-said materials. Typical examples of such additives  
are tertiary amines such as triethanolamine when used  
in combination with benzophenone. Such sensitizer and/or  
5 sensitizer system is preferably contained in an amount  
of 0.5 to 10% by weight in the photosensitive resin  
composition.

The photosensitive resin composition according  
to this invention may also contain one or more other  
10 secondary components such as, for example, thermal poly-  
merization inhibitors, dyes, pigments, fillers, dispersion  
stabilizers, coating property improvers, flame retardants,  
flame-retardant assistants, etc. These additives may  
be properly selected in the same way as used with the  
15 ordinary photosensitive resin compositions.

Now, the ways of use of the photosensitive  
resin composition of this invention are described by  
way of examples thereof.

Formation of a layer of the photosensitive resin  
20 composition of this invention on a substrate may be  
accomplished in a usual way. For example, such layer  
may be formed by uniformly dissolving the photosensitive  
resin composition in an organic solvent such as methyl  
ethyl ketone, toluene, methylene chloride, etc. (with the  
25 filler, pigment, etc., being uniformly dispersed),  
then directly applying this solution on the substrate  
by dip coating, flow coating or other means and then  
drying the solvent. Thereafter, said layer is exposed

1 imagewise to a light source such as an ultra-high pressure  
mercury arc lamp through a negative mask, either directly  
or after further providing on said photosensitive  
resin layer an oxygen-impermeable protective layer such  
5 as shown in Japanese Patent Appln Kokoku (Post-Exam  
Publn) Nos. 35687/71 and 32714/71 or laminating a film  
pervious to actinic light such as a polyester film. In  
case a polyester film or such is laminated, development  
is conducted after removing such film. As the developing  
10 solution, there may be used an organic solvent such as  
1,1,1-trichloroethane, an alkaline aqueous solution, an  
aqueous solution of an organic solvent and the like.

The development is followed by a heat treatment  
at a temperature of 80° to 200°C and exposure to actinic  
15 light, whereby a soldering mask with excellent properties  
can be obtained. As for the order of said heat treatment  
and exposure to actinic light to be performed after  
development, either of them may come first, and also  
each of these treatments may be conducted in several  
20 stages. The protective coating film obtained as a result  
of such heat treatment and exposure to actinic light  
after development shows excellent soldering heat resist-  
ance. Also, this protective film is well resistant to  
the organic solvents such as trichloroethylene, isopropyl  
25 alcohol, toluene, etc., as well as to the acidic and  
alkaline solutions, so that it can be used as a permanent  
protective film for soldering masks, etc.

Further, the photosensitive resin composition

- 1 of this invention may be printed imagewisely on a substrate by silk screen printing and then photoset by using a light source such as a high pressure mercury arc lamp to form an image-patterned protective coating film.
- 5 The thus obtained protective coating film also has excellent adhesiveness to the substrate surface.

The photosensitive element according to this invention has a structure such as illustrated in Fig. 1 of the accompanying drawings, and such an element can

10 be obtained by forming a layer 19 of said photosensitive resin composition on a support film 18 in the substantially same way as the above-described operations. Formation of the photosensitive resin composition layer on the support film can be accomplished in a usual way.

15 For instance, the photosensitive resin composition is uniformly dissolved in an organic solvent such as methyl ethyl ketone, toluene, methylene chloride, etc. (with pigments, etc., being uniformly dispersed) and this solution is applied on the support film by suitable

20 means such as knife coating, roll coating, etc., and dried. It is desirable that the amount of the residual solvent in the photosensitive layer is kept 2% by weight or less, most preferably 1% by weight or less, for maintaining the properties of the composition.

25 The support film used in this invention may be either pervious or impervious to actinic light. Preferred examples of such support film are polyester film, polyimide film, polystyrene film and other like known

1 films.

In case of producing a long photosensitive element, said element is wound up into a roll in the final stage of production. In this case, it is possible to prevent the photosensitive resin composition layer in the rolled element from adhering to the back side of the support film by using a support film whose back side has been properly treated by a method known in the art of production of pressure-sensitive adhesive tapes. It is also desirable to laminate a strippable cover film 20 on the photosensitive resin composition layer 19 of said element for the same purpose and/or other purposes such as prevention of deposition of dust.

Examples of such strippable cover film are polyethylene film, polypropylene film, Teflon<sup>(RTM)</sup> film, surface-treated paper and the like, but such cover film should be one whose adhesive force to the photosensitive resin composition layer proves to be smaller than the adhesive force between the photosensitive resin composition layer and the support film when said cover film is stripped off.

Now, the applications of the photosensitive element according to this invention are illustrated by way of the following Examples.

25 Lamination of the photosensitive element of this invention on a substrate is easy. When no cover film is provided, said element can be immediately laminated on the substrate by heating it under pressure, and when

1 a cover film is provided, said element is similarly  
laminated after or while stripping off the cover film.  
Such heat-and-pressure lamination can be accomplished  
by using a normal-pressure laminator well known to the  
5 printed wiring board manufactures. In case the substrate  
is of the type which has unevenness of more than 10  $\mu\text{m}$   
as in a printed wiring board formed with conductor  
wiring lines, it is preferred to perform said lamination  
under reduced pressure or in vacuo. As means for ef-  
10 fectuating such lamination, there may be used, for  
example, the laminators disclosed in Japanese Patent  
Appln Kokai (Laid-Open) No. 52703/77 and U.S. Patent  
No. 4,127,436.

Exposure and development after lamination can  
15 be performed in a usual way. For instance, in case the  
support film is impervious to actinic light, such support  
film is first stripped off and then the laminate is  
exposed imagewisely through a negative mask by using a  
light source such as a high pressure mercury arc lamp  
20 or an ultra-high pressure mercury arc lamp.

In case the support film still remains after  
exposure, such remaining support film is removed and  
then development is conducted. An organic solvent such  
as 1,1,1-trichloroethane, an alkaline aqueous solution,  
25 an aqueous solution of an organic solvent and the like  
may be used as the developing solution.

An additional heat treatment at 80° to 200°C  
and further exposure to actinic light provide a soldering

- 1 mask with excellent properties. Either of such post-development heat treatment and exposure to actinic light may be conducted ahead of the other, and also each of such treatments may be performed in several stages.
- 5 The protective film obtained by such post-development heat treatment and exposure to actinic light exhibits excellent soldering heat resistance. Further, such protective film is well resistant to organic solvents such as tri-chloroethylene, isopropyl alcohol, toluene, etc., as well
- 10 as to the acidic and alkaline aqueous solutions, so that it can be advantageously used as a permanent protective film for soldering masks, etc.

The present invention is further described hereinbelow by way of the following Examples and Compara-

15 tive Examples, wherein all "parts" and "percents" are by weight unless otherwise specified.

**Example 1**

- (a) Synthesis of a photopolymerizable compound having a terminal ethylene group

**Materials**

|                                       |                             |
|---------------------------------------|-----------------------------|
| A Trimethylhexamethylene diisocyanate | 1155 parts (11 equivalents) |
| Isophorone diisocyanate               | 555 parts (5 equivalents)   |
| Toluene                               | 1200 parts                  |
| Di-n-butyltin dilaurate               | 1 part                      |

|   |                         |                                |
|---|-------------------------|--------------------------------|
| B | 2-Hydroxyethyl acrylate | 1624 parts<br>(14 equivalents) |
|   | 1,4-Butanediol          | 90 parts (2<br>equivalents)    |
|   | Toluene                 | 300 parts                      |
|   | p-Methoxyphenol         | 0.3 part                       |
| C | Methanol                | 20 parts                       |

1            Said material A was placed in an approximately  
5-litre-capacity heatable and coolable reactor equipped  
with a thermometer, a stirrer, a cooling pipe, a nitrogen  
gas feed pipe and a dropper, and said material A was  
5 heated to 60°C under stirring. Then material B was added  
dropwise uniformly into said material A in the reactor  
over a period of about 5 hours while maintaining the  
reaction temperature at 55 - 65°C. After addition of B,  
the reaction temperature was raised gradually to 80°C  
10 over a period of about 5 hours. Thereafter, the tempera-  
ture was lowered to 60°C and material C was added, follow-  
ed by about one-hour stirring of the mixture. Then the  
reaction mixture was dried under reduced pressure to  
remove the solvent, thereby obtaining a viscous photo-  
15 polymerizable compound (I) having a terminal ethylene  
group.

1 (b) Production of photosensitive element

Materials

|                                                                                                                                                |           |
|------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| Photopolymerizable compound (I)<br>obtained by the above-said method                                                                           | 40 parts  |
| A-TMPT (a polyvalent acrylate<br>manufactured by Shin-Nakamura<br>Kagaku K.K.)                                                                 | 10 parts  |
| Methyl methacrylate/methyl<br>acrylate/acrylic acid/acrylo-<br>nitrile (83/10/2/5 by weight)<br>copolymer (molecular weight:<br>about 120,000) | 50 parts  |
| Benzophenone                                                                                                                                   | 2.7 parts |
| Michler's ketone                                                                                                                               | 0.3 part  |
| p-Methoxyphenol                                                                                                                                | 0.02 part |
| Victoria pure blue                                                                                                                             | 0.05 part |
| Toluene                                                                                                                                        | 50 parts  |
| Methyl ethyl ketone                                                                                                                            | 50 parts  |

Hydroxybenzotriazole and PHOSMER-M (a trade name of a phosphate compound containing a methacryl group, manufactured by Yushi Seihin Co., Ltd.) were added in amounts shown in Table 1 to 20 parts of the blend of the above-shown materials to prepare 10 types (specimens) of solutions of photosensitive resin composition.

Table 1

| Run No. | Amount of hydroxy-benzotriazole added (part) | Amount of PHOSMER-M. added (part) |
|---------|----------------------------------------------|-----------------------------------|
| EX-1    | 0                                            | 0                                 |
| EX-2    | 0.005                                        | 0                                 |
| EX-3    | 0.020                                        | 0                                 |
| EX-4    | 0.100                                        | 0                                 |
| EX-5    | 0                                            | 0.005                             |
| EX-6    | 0                                            | 0.020                             |
| EX-7    | 0                                            | 0.100                             |
| EX-8    | 0.003                                        | 0.020                             |
| EX-9    | 0.010                                        | 0.010                             |
| EX-10   | 0.010                                        | 0.005                             |

(Note) Figures are added amounts in part to 20 parts of the blend of the above-shown composition.

- 1 By using the apparatus shown in Fig. 3, each of said ten types of photosensitive resin composition solutions 10 was applied uniformly on a 25  $\mu$ m thick polyethylene terephthalate film 16 and dried by passing
- 5 it through a 80 - 100°C hot air convection dryer 11 for about 10 minutes. The thickness of the photosensitive resin composition layer after drying was about 75  $\mu$ m. An about 25  $\mu$ m thick polyethylene film 17 was pasted on the photosensitive resin composition layer as a cover
- 10 film as shown in Fig. 3.

1            In Fig. 3, reference numeral 5 indicates a  
polyethylene terephthalate film delivering roll, 6, 7  
and 8 rolls, 9 a knife, 12 a polyethylene film deliver-  
ing roll, 13 and 14 rolls, and 15 a photosensitive  
5 element take-up roll.

(c) Formation of soldering mask

Each of the 10 specimens of photosensitive  
element obtained in (b) above was laminated on a copper-  
clad laminate (MCL-E 61 mfd. by Hitachi Chemical Co., Ltd.,  
10 copper foil thickness: 35  $\mu$ m, substrate thickness:  
1.6 mm) with its copper surface cleaned by a pretreatment  
while stripping off the cover film by using laminator  
A-500 mfd. by Akebono Industry Co., Ltd. After lamination,  
the laminate was irradiated with ultraviolet rays at  
15 an exposure rate of 150 mJ/cm<sup>2</sup> through a negative mask  
for test shown in Fig. 4 by using an exposing machine  
PHENIX-3000 mfd. by ORC Factory Co., Ltd. In Fig. 4,  
numeral 3 indicates the opaque portion of the negative  
mask and 4 the transparent portion. The unit of the  
20 figures is mm.

After standing at room temperature for 30  
minutes, the support film was stripped off and the  
laminate was subjected to spray development at 20°C for  
120 seconds by using 1,1,1-trichloroethane. After  
25 development, the laminate was dried with heating at  
80°C for 10 minutes, then further subjected to a 30-minute  
heat treatment at 150°C and then irradiated with ultra-

- 1 violet rays for an exposure of  $5 \text{ J/cm}^2$  by using an ultraviolet irradiator manufactured by Toshiba Denzai Co., Ltd.

The thus obtained ten test substrates formed with a protective coating film were then subjected to a soldering test by contacting them with a  $255 - 265^\circ\text{C}$  flow soldering bath for 30 seconds by using a rosin type flux A-226 (manufactured by Tamura Kaken Co., Ltd.). The results are shown collectively in Table 2.

Table 2

| Run No. | Condition of protective film           |
|---------|----------------------------------------|
| EX-1    | Poor as floating and peel-off occurred |
| EX-2    | Ditto                                  |
| EX-3    | Ditto                                  |
| EX-4    | Ditto                                  |
| EX-5    | Ditto                                  |
| EX-6    | Ditto                                  |
| EX-7    | Ditto                                  |
| EX-8    | Good                                   |
| EX-9    | Good                                   |
| EX-10   | Good                                   |

- 10 As is clear from Table 2, only the protective films formed from the photosensitive element specimens containing both hydroxybenzotriazole and PHOSMER-M

- 1 (EX-8, EX-9 and EX-10) showed excellent soldering heat resistance, while the protective films formed from other specimens, that is, the specimen containing neither hydroxybenzotriazole nor PHOSMER-M (EX-1),
- 5 the specimens containing hydroxybenzotriazole but not containing PHOSMER-M (EX-2, EX-3 and EX-4) and the specimens containing PHOSMER-M but not containing hydroxybenzotriazole (EX-5, EX-6 and EX-7), suffered from excessive floating or peel-off in said soldering test
- 10 and also soldering penetrate was seen in these protective films.

#### Example 2

##### Materials

|                                                                                                                                                  |          |
|--------------------------------------------------------------------------------------------------------------------------------------------------|----------|
| Photopolymerizable compound (I) having a terminal ethylene group synthesized in Example 1-(a)                                                    | 40 parts |
| ARONIX M-6100 (a trade name of a polyvalent acrylate manufactured by Toagosei Chemical Industry Co., Ltd.)                                       | 12 parts |
| Methyl methacrylate/ethyl acrylate/tetrahydrofurfuryl methacrylate/tribromophenyl acrylate (60/4/10/26 by weight) copolymer (M.W. about 100,000) | 48 parts |
| Benzophenone                                                                                                                                     | 4 parts  |
| Michler's ketone                                                                                                                                 | 0.2 part |
| Benzimidazole                                                                                                                                    | 0.1 part |
| KAYAMER-PA2 (a trade name for a phosphate compound containing an acryl group mfd. by Nippon Kayaku Co., Ltd.)                                    | 0.2 part |

|                                                                                          |          |
|------------------------------------------------------------------------------------------|----------|
| Phthalocyanine Green SAX (a trade name for a pigment manufactured by Sanyo Shikiso K.K.) | 0.3 part |
| Antimony trioxide                                                                        | 1 part   |
| Methyl ethyl ketone                                                                      | 10 parts |
| Toluene                                                                                  | 50 parts |

1           A printed wiring board for test (with a glass epoxy substrate having a thickness of 1.6 mm) formed with a copper pattern (approximately 50  $\mu$ m thick) shown in Fig. 5 was immersed in a solution of the photosensitive resin composition consisting of the above-shown materials and then dried at 80°C for 20 minutes to form on the surface of said printed wiring board a layer of the photosensitive resin composition with a thickness after drying of about 60  $\mu$ m. In Fig. 5, numeral 1 designates the copper pattern portion and 2 the exposed portion of the substrate, and the unit of the figures is mm. On the photosensitive resin composition layer was further laminated an approximately 25  $\mu$ m thick polyethylene terephthalate film. The laminate was then exposed to ultraviolet rays at a rate of 120 mJ/cm<sup>2</sup> through a testing negative mask shown in Fig. 4. After allowing the laminate to stand at room temperature for 30 minutes, the polyethylene terephthalate film was stripped off, followed by 120-second spray development with 1,1,1-trichloroethane. After development, the laminate was dried under heating at 80°C for 10 minutes and the irradiated with ultraviolet rays for an exposure

1 of 3 J/cm<sup>2</sup>, which was further followed by a 30-minute  
heat treatment at 160°C. The thus obtained test sub-  
strate formed with a protective film was subjected to  
the soldering test by contacting it for 15 seconds with  
5 a 255 - 265°C flow soldering bath by using a rosin type  
flux MH-320V (mfd. by Tamura Kaken Co., Ltd.). This  
substrate remained free of floating and peel-off of  
the protective film and showed excellent soldering heat  
resistance.

10 Comparative Example 1

In the same way as Example 2 except for non-  
use of KAYAMER-PA2, a photosensitive element was produced,  
then an imagewise protective film was formed on the  
test substrate and the element was subjected to the  
15 soldering test. Floating and blistering were admitted  
in the protective film and also solder penetrating  
occured.

Example 3

Materials

|                                                                                                                                                 |          |
|-------------------------------------------------------------------------------------------------------------------------------------------------|----------|
| ARONIX M-8060 (polyvalent acrylate mfd.<br>by Toagosei Chemical Industry Co., Ltd.)                                                             | 15 parts |
| AECHPP (a trade name of a monovalent<br>acrylate mfd. by Osaka Yuki K.K.)                                                                       | 5 parts  |
| A-TMM-3L (a trade name of a polyvalent<br>acrylate mfd. by Shin-Nakamura Kagaku K.K.)                                                           | 30 parts |
| Methyl methacrylate/methyl acrylate/<br>methacrylic acid/tribromophenyl<br>acrylate (70/10/10/10 by weight) co-<br>polymer (MW. approx. 70,000) | 50 parts |

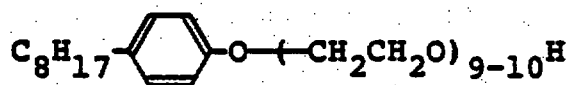
|                                                                                                |           |
|------------------------------------------------------------------------------------------------|-----------|
| Benzophenone                                                                                   | 4 parts   |
| Michler's ketone                                                                               | 0.2 part  |
| Benzotriazole hydrochloride                                                                    | 0.05 part |
| PHOSMER-CL (a phosphate compound containing a methacryl group, mfd. by Yushi Seihin Co., Ltd.) | 0.1 part  |
| Victoria Pure Blue                                                                             | 0.01 part |
| Phthalocyanine Green SAX                                                                       | 0.2 part  |
| Antimony trioxide                                                                              | 2 parts   |
| Ethyl Cellosolve (RTM)                                                                         | 40 parts  |
| Methyl ethyl ketone                                                                            | 30 parts  |

1           A solution of the photosensitive resin composition of the above-shown recipe was applied on a testing printed wiring board (with a glass epoxy substrate having a thickness of 1.2 mm) formed with a copper

5   pattern (with a copper thickness of about 35  $\mu\text{m}$ ) shown in Fig. 5 and then dried at 90°C for 15 minutes. The thickness of the photosensitive resin composition layer after drying was about 50  $\mu\text{m}$ .

Then this photosensitive resin composition

10   layer was further coated with a 3% aqueous solution of polyvinyl alcohol (saponification degree: 99%) containing 2% of a polyoxyethylene surfactant of the formula:



and dried at 105°C for 5 minutes. The post-drying

1 thickness of the polyvinyl alcohol coating was about 1  $\mu$ m.

This was then irradiated with ultraviolet rays at an exposure of 180 mJ/cm<sup>2</sup> through a testing negative mask shown in Fig. 4, allowed to stand at room  
5 temperature for 30 minutes and then subjected to 120-second spray development with a developing solution of the composition shown below to thereby remove the polyvinyl alcohol coating and the unexposed portion of the photosensitive layer. After washing with water, the  
10 resulting substrate was dried under heating at 80°C for 15 minutes, then irradiated with ultraviolet rays at an exposure rate of 3 J/cm<sup>2</sup> and further subjected to a 30-minute heat treatment at 160°C.

The thus obtained test substrate with a protective film was subjected to the soldering test by  
15 contacting it for 15 seconds with a 255 - 265°C flow soldering bath by using a water-soluble flux WS-37 (mfd. by Tamura Kaken Co., Ltd.). This substrate suffered no floating nor peel-off of the protective film and  
20 showed good soldering heat resistance.

#### Example 4

- (a) Synthesis of a photopolymerizable compound having a terminal ethylene group

##### Materials

|                                       |                                |
|---------------------------------------|--------------------------------|
| A Trimethylhexamethylene diisocyanate | 1680 parts<br>(16 equivalents) |
| Toluene                               | 1200 parts                     |

|                           |                                |
|---------------------------|--------------------------------|
| Di-n-butyltin dilaurate   | 1 part                         |
| B 2-Hydroxyethyl acrylate | 1856 parts<br>(16 equivalents) |
| Toluene                   | 300 parts                      |
| p-Methoxyphenol           | 0.3 part                       |
| C Methanol                | 20 parts                       |

- 1 By using the above-shown materials, there was prepared a viscous photopolymerizable compound (II) having a terminal ethylene group in the same way as Example 1.

- 5 (b) Production of photosensitive elements and formation of soldering mask

Materials

|                                                                                                                      |           |
|----------------------------------------------------------------------------------------------------------------------|-----------|
| Photopolymerizable compound (II) obtained in the manner described above                                              | 50 parts  |
| Methyl methacrylate/methyl acrylate/acrylic acid/acrylonitrile (83/10/2/5 by weight) copolymer (MW. approx. 120,000) | 50 parts  |
| Benzophenone                                                                                                         | 2.7 parts |
| Michler's ketone                                                                                                     | 0.3 part  |
| p-Methoxyphenol                                                                                                      | 0.02 part |
| Victoria Pure Blue                                                                                                   | 0.05 part |
| Toluene                                                                                                              | 50 parts  |
| Methyl ethyl ketone                                                                                                  | 50 parts  |

- 10 Benzotriazole and PHOSMER-M (a phosphate compound containing a methacryl group mfd. by Yushi

- 1 Seihin Co., Ltd.) were added in amounts shown in Table 3 to 20 parts of the blend of the above-shown composition to prepare 10 solutions of photosensitive resin compositions.

Table 3

| Run No. | Amount of benzotriazole added (part) | Amount of PHOSMER-M added (part) |
|---------|--------------------------------------|----------------------------------|
| EX-11   | 0                                    | 0                                |
| EX-12   | 0.005                                | 0                                |
| EX-13   | 0.020                                | 0                                |
| EX-14   | 0.100                                | 0                                |
| EX-15   | 0                                    | 0.005                            |
| EX-16   | 0                                    | 0.020                            |
| EX-17   | 0                                    | 0.100                            |
| EX-18   | 0.003                                | 0.020                            |
| EX-19   | 0.010                                | 0.010                            |
| EX-20   | 0.010                                | 0.005                            |

(Note) Figures are added amount in part to 20 parts of the blend of the above-shown composition.

- 5 By using these 10 solutions of photosensitive resin compositions, there were produced the photosensitive elements and further the soldering masks were formed in the same way as Example 1, and they were subjected to the same soldering test as conducted in Example 1.
- 10 The results are collectively shown in Table 4.

Table 4

| Run No. | Condition of protective film           |
|---------|----------------------------------------|
| EX-11   | Poor as floating and peel-off occurred |
| EX-12   | Ditto                                  |
| EX-13   | Ditto                                  |
| EX-14   | Ditto                                  |
| EX-15   | Ditto                                  |
| EX-16   | Ditto                                  |
| EX-17   | Ditto                                  |
| EX-18   | Good                                   |
| EX-19   | Good                                   |
| EX-20   | Good                                   |

1           As seen from Table 4, only the protective  
films formed from the photosensitive elements containing  
both benzotriazole and PHOSMER-M (EX-18, EX-19 and EX-20)  
showed good soldering heat resistance, while the pro-  
5   tective films formed from other photosensitive elements,  
that is, the element containing neither benzotriazole  
nor PHOSMER-M (EX-11), the elements containing benzo-  
triazole but not containing PHOSMER-M (EX-12, EX-13  
and EX-14) and the elements containing PHOSMER-M but  
10 not containing benzotriazole (EX-15, EX-16 and EX-17),  
suffered excess floating or peel-off in said soldering  
test, and also solder penetrating was seen in these  
protective films.

1 Example 5

Materials

|                                                                                                                                                               |          |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------|----------|
| Photopolymerizable compound (II)<br>having terminal ethylene group synthesized<br>in Example 4-(a)                                                            | 40 parts |
| ARONIX M-8060 (a polyvalent acrylate<br>mfd. by Toagosei Chemical Industry<br>Co., Ltd.)                                                                      | 12 parts |
| Methyl methacrylate/ethyl acrylate/<br>tetrahydrofurfuryl methacrylate/<br>tribromophenyl acrylate<br>(60/4/10/26 by weight) copolymer<br>(MW. about 100,000) | 48 parts |
| Benzophenone                                                                                                                                                  | 4 parts  |
| Michler's ketone                                                                                                                                              | 0.2 part |
| Benzimidazole                                                                                                                                                 | 0.1 part |
| KAYAMER-PA2 (a phosphate compound<br>containing an acryl group mfd. by<br>Nippon Kayaku Co., Ltd.)                                                            | 0.2 part |
| Phthalocyanine Green SAX (a pigment<br>mfd. by Sanyo Shikiso K.K.)                                                                                            | 0.3 part |
| Antimony trioxide                                                                                                                                             | 1 part   |
| Methyl ethyl ketone                                                                                                                                           | 60 parts |
| Toluene                                                                                                                                                       | 50 parts |

A solution of the photosensitive resin composition containing the above-shown materials was uniformly applied on a 25  $\mu$ m thick polyethylene terephthalate film by using the apparatus shown in Fig. 3 and then dried by passing through a 80 - 100°C hot air convection dryer for about 12 minutes. The photosensitive resin composition layer formed after drying had a thickness of about 90  $\mu$ m. On this photosensitive resin composition

1 layer was further pasted an about 25  $\mu$ m thick polyethylene  
film 17 as cover film as shown in Fig. 3. The thus  
obtained photosensitive element was heat laminated  
under pressure, while stripping off the cover film,  
5 on a test printed wiring board (with a glass epoxy  
substrate having a thickness of 1.6 mm) having formed  
thereon a copper pattern (with a copper buildup of about  
70  $\mu$ m) shown in Fig. 5, by using a vacuum laminator  
mfd. by Hitachi Chemical Co., Ltd., (a degree of vacuum:  
10 30 mm Hg, laminating temperature: 100°C, laminating  
speed: 1 m/min). In Fig. 5, reference numeral 1  
denotes the copper pattern portion and 2 the exposed  
portion of the substrate, and the unit of the figures  
is mm. The laminate was allowed to stand at room temper-  
15 ature for 3 hours and then irradiated with ultraviolet  
rays at an exposure of 150 mJ/cm<sup>2</sup> through a test negative  
mask shown in Fig. 4. After additional 30-minute  
standing at room temperature, the support film was strip-  
ped off and the laminate was spray-developed at 20°C  
20 for 150 seconds by using 1,1,1-trichloroethane. After  
the development, the laminate was dried with heating  
at 80°C for 10 minutes, again irradiated with ultraviolet  
rays to effect 3 J/cm<sup>2</sup> exposure and further subjected  
to a heat treatment at 150°C for 30 minutes. The thus  
25 obtained test substrate formed with a protective film  
was subjected to the soldering test by contacting it  
for 15 seconds with a 255 - 265°C flow soldering bath  
using a rosin type flux MH-320V (mfd. by Tamura Kaken

- 1 Co., Ltd.). No floating nor peel-off of the protective film occurred, indicating excellent soldering heat resistance of this substrate.

#### Comparative Example 2

- 5           The process of Example 5 was repeated except for not adding KAYAMER-PA2, a photosensitive element was produced. Then this element was laminated on a test substrate and an image-like protective film was formed thereon, and the thus obtained substrate was  
10 subjected to the same soldering test as in Example 5. Floating and blistering of the protective film occurred, and also solder penetrating took place.

#### Example 6

##### Materials

|                                                                                                                                             |           |
|---------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| ARONIX M-6100 (a polyvalent acrylate mfd. by Toagosei Chemical Industry Co., Ltd.)                                                          | 15 parts  |
| MECHPP (a monovalent methacrylate mfd. by Osaka Yuki K.K.)                                                                                  | 5 parts   |
| A-TMM-3L (a polyvalent acrylate mfd. by Shin-Nakamura Kagaku K.K.)                                                                          | 20 parts  |
| Methyl methacrylate/ethyl acrylate/styrene/methacrylic acid/tribromophenyl acrylate (35/20/10/25/10 by weight) copolymer (MW. about 80,000) | 60 parts  |
| Benzophenone                                                                                                                                | 4 parts   |
| Michler's ketone                                                                                                                            | 0.2 part  |
| Benzotriazole hydrochloride                                                                                                                 | 0.05 part |

PHOSMER-CL (a phosphate compound  
containing a methacryl group mfd. by  
Yushi Seihin Co., Ltd.)

0.1 part

Victoria Pure Blue

0.01 part

Antimony trioxide

1 part

Ethyl Cellosolve

80 parts

Methyl ethyl ketone

40 parts

- 1 By using a solution of the photosensitive  
resin composition of the above-shown recipe, there  
was produced a photosensitive element having an approxi-  
mately 60  $\mu\text{m}$  thick photosensitive resin composition layer  
5 in the same way as Example 5. This photosensitive  
element was heat laminated under reduced pressure  
(a degree of vacuum: 20 mm Hg), while stripping off  
the cover film, on a test printed wiring board (with  
a glass epoxy substrate having a thickness of 0.8 mm)  
10 formed with a copper pattern (with a copper buildup  
of about 35  $\mu\text{m}$ ) shown in Fig. 5. After standing at  
room temperature for 24 hours, the laminate was irradiat-  
ed with ultraviolet rays at an exposure of 150  $\text{mJ}/\text{cm}^2$   
through a test negative mask shown in Fig. 4. After  
15 additional 30-minute standing at room temperature, the  
support film was stripped off and the laminate was  
developed by spraying a 2% aqueous solution of sodium  
carbonate of 35°C for 70 seconds.

- After washing with water, the laminate was  
20 dried with heating at 80°C for 20 minutes, then irradiated  
with ultraviolet rays at an exposure rate of 3  $\text{J}/\text{cm}^2$

- 1 and further subjected to a 40-minutes heat treatment  
at 160°C.

The thus obtained test substrate formed with  
a protective film was subjected to the soldering test  
5 by contacting it for 15 seconds with a 255 - 265°C flow  
soldering bath by using a water-soluble flux WS-37  
(mfd. by Tamura Kaken Co., Ltd.). This substrate caused  
no floating nor peel-off of the protective film and  
exhibited excellent soldering heat resistance.

- 10 As explained in detail in the Examples, it is  
quite surprising that the soldering heat resistance  
is amazingly improved only when using in combination  
two different types of components (a) and (b) which,  
when used independently, show no noticeable effect even  
15 if the blended amount is increased. The photosensitive  
resin composition and the photosensitive element accord-  
ing to this invention can form a protective film with  
excellent adhesiveness to the substrate surface, and  
the formed protective film is suited for use as a  
20 resist for soldering mask, etc.

CLAIMS

1. A photosensitive resin composition comprising:

(a) at least one benzotriazole, benzimidazole or benzothiazole or derivative thereof as herein defined or salt thereof,

(b) a phosphate compound having at least one photopolymerizable unsaturated bond,

(c) optionally, an organic thermoplastic polymer,

(d) a photopolymerizable unsaturated compound having at least one terminal ethylene group, and

(e) a sensitizer and/or a sensitizer system capable of initiating polymerization of said unsaturated compounds (b) and (d) upon irradiation with actinic light.

2. A composition according to claim 1, wherein the component (a) is contained in an amount of about 0.001% by weight or more, and the component (b) in an amount of about 0.001% by weight or more, based on the weight of the photosensitive resin composition, the component (c) is contained, when present, in an amount of 20 to 80 parts by weight, the component (d) is contained in an amount of 20 to 80 parts by weight and the component (e) is contained in an amount of 0.5 to 10% by weight.

3. A composition according to claim 1 or 2 wherein the derivative of benzotriazole, benzimidazole or benzothiazole is one having one or more alkyl groups, aryl groups, nitro groups, amino groups, hydroxyl groups, carboxyl groups or halogens substituted for hydrogen.



4. A composition according to claim 1 or 2 wherein the salt of benzotriazole, benzimidazole or benzothiazole is an acid salt or an amine salt.

5. A composition according to any one of the preceding claims wherein component (b) is at least one compound which is acid phosphoxyethyl methacrylate, 3-chloro-2-acid phosphoxypropyl methacrylate, bis(methacryloxyethyl)phosphate, acryloxyethyl phosphate and bis(acryloxyethyl)phosphate.

6. A composition according to any one of the preceding claims, wherein component (c) is a vinyl copolymer.

7. A composition according to any one of the preceding claims, wherein component (d) is an urethane diacrylate or urethane dimethacrylate compound obtained by reacting:

(i) trimethylhexamethylene diisocyanate and/or isophorone diisocyanate,

(ii) an acrylic or methacrylic monoester of a dihydric alcohol, and optionally

(iii) a dihydric alcohol.

8. A composition according to any one of the preceding claims, wherein the component (a) is hydroxy-benzotriazole and the component (b) is acid phosphoxyethyl methacrylate.



9. A composition according to any one of claims 1 to 7, wherein the component (a) is benzimidazole and the component (b) is bis(acryloxyethyl)phosphate.

10. A composition according to any one of claims 1 to 7, wherein the component (a) is benzotriazole hydrochloride and the component (b) is 3-chloro-2-acid phosphoxypropyl methacrylate.

11. A composition according to claim 1, substantially as hereinbefore described with reference to any one of the Examples.

12. A photosensitive element comprising a layer of a photosensitive resin composition according to any one of the preceding claims and including component (c) and a support film supporting said layer.

13. A photosensitive element according to claim 12 substantially as hereinbefore described with reference to any one of the Examples.

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