

DESCRIPTION

The present invention relates to novel 1,3-diaza-9-thia-anthracene-2,4-diones and to a photopolymerizable mixture which contains, as the essential components,

- a) a polymeric binder
- b) a polymerizable compound having at least two terminal, ethylenically unsaturated groups and a boiling point of more than 100°C, and
- c) a 1,3-diaza-9-thia-anthracene-2,4-dione as the photoinitiator.

Photopolymerizable mixtures which contain the components a) and b) and a polynuclear heterocyclic compound as the photoinitiator are known.

In DE-C 20 27 467 (= GB-A 1,354,541) specific derivatives of acridine and phenazine are described as initiators.

DE-C 20 39 361 (= US-A 3,765,898) discloses similar mixtures containing quinoxaline derivatives or quinazoline derivatives as initiators.

All these compounds have an excellent initiator effect when they are irradiated with actinic light, in particular of light sources emitting in the near ultraviolet range. But in recent times, metal halide-doped gas

discharge lamps have become more and more customary for copying purposes because of their high luminous efficiency, and as these lamps have stronger emission values in the range of the visible light of more than 400 nm than the hitherto conventionally used light sources, such as e.g. mercury vapor lamps, the absorption values of the known highly efficient initiators are no longer matched to the emissions of these light sources in the best possible way. Moreover, the variation possibilities by substitution of the known heterocyclic initiators are limited, i.e. , by means of the known production processes it is possible to a limited degree only to modify other properties, if desired, such as solubility in aqueous or organic solvents or compatibility with various photopolymerizable mixtures, by a purposeful synthesis.

In Journ. of Heterocyclic Chemistry 18, p. 1,329 (1981), 1-3-diaza-9-thia-anthracene-2,4-diones are described which in their 6-position are either unsubstituted or substituted by a chlorine atom or a methyl group. In the publication, these components are tested for their oxidation capacity in respect of alcohols. Other applications are not mentioned.

It was therefore the object of the present invention to propose novel photoinitiators which possess a similarly high efficiency as the known photoinitiators, while their light absorption extends more deeply into the short-wave visible range, and into which specific substi-

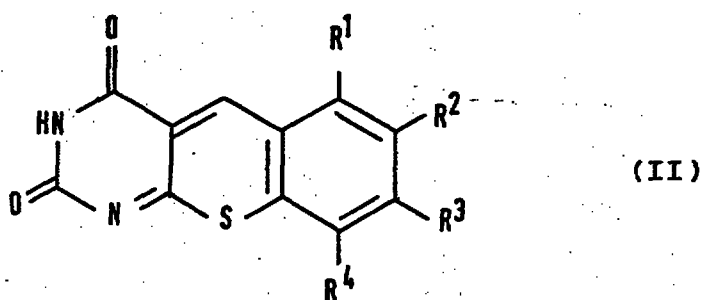
- 3 -

tuents can be purposefully introduced in the course of their synthesis, which impart various, desired properties, such as solubility and compatibility with other components, to the final products.

The subject of this invention is a photopolymerizable mixture which contains, as essential constituents,

- a) a polymeric binder
- b) a polymerizable compound having at least two terminal, ethylenically unsaturated groups and a boiling point of more than 100°C, and
- c) a polynuclear N-heterocyclic compound as photoinitiator.

The mixture of the invention is characterized in that the N-heterocyclic compound corresponds to the general formula (II)

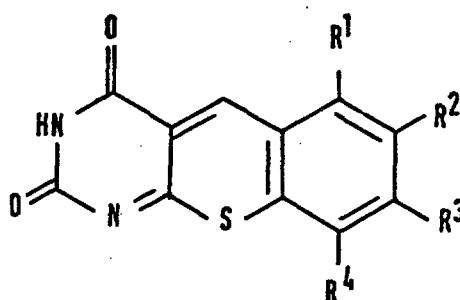


in which

R¹, R², R³ are identical or different and individually
and R⁴ each denote a hydrogen or halogen atom, a

carboxyl group, an alkyl, alkoxy or alkoxy-carbonyl group, whereby each of the alkyl groups contains 1 to 6 carbon atoms, or two of the groups R^1 to R^4 each denote a fused aromatic radical.

In accordance with this invention, there are further proposed novel 1,3-diaza-9-thia-anthracene-2,4-diones of the general formula (II)



(II)

in which

R^1 , R^3
and R^4

are identical or different and individually each denote a hydrogen or halogen atom, a carboxyl group, an alkyl, alkoxy or alkoxy-carbonyl group, whereby each of the alkyl groups contains 1 to 6 carbon atoms, and

R^2

denotes a carboxyl, alkoxy or alkoxy-carbonyl group, whereby each of the alkoxy groups contains 1 to 6 carbon atoms, or two of the radicals

R^1 , R^2 , R^3
and R^4

each denote a fused aromatic radical.

The novel compounds can be prepared following the way diagrammatically indicated in the attached Figure.

They absorb light in a spectral range of from about 425 to 480 nm and, when being irradiated in this spectral range, act as active radical initiators of the photopolymerization of vinyl compounds, even in the presence of oxygen. The novel photoinitiators do not initiate the thermal polymerization of such compounds when there is no actinic radiation. Therefore, they are very well suitable for the preparation of storable copying layers.

It is of advantage that the compounds (II) can be produced by smooth reactions and using readily accessible educts known from literature, that the substituents $R^1 - R^4$ can be varied within a wide range, and that purification operations are necessary during the final stage only.

The alkyl and alkoxy groups which can be used as possible substituents preferably have 1 to 3 carbon atoms; methyl and methoxy groups are particularly preferred.

Fluorine, chlorine and bromine atoms, in particular chlorine atoms, are the preferred halogen atoms. The alkoxy groups of the alkoxy-carbonyl groups may be the same as stated above. Benzo radicals are the particularly preferred condensed aromatic radicals.

Of the compounds according to the general formula II, particular preference is given to those, wherein at least one of the radicals R^1 to R^4 is a hydrogen atom. Compounds, wherein two or three of these radicals, particularly of the radicals R^1 to R^3 , are hydrogen atoms, are

especially preferred. If two of the radicals denote a benzo group, the two remaining radicals are preferably hydrogen atoms.

The added amount of photoinitiators in general varies between 0.01 and 10, preferably between 0.1 and 5 % by weight, relative to the components of the photopolymerizable layer.

Photopolymerizable monomers useful for the purposes of this invention are known and are, for example, described in U.S. Patents No. 2,760,863 and 3,060,023. Preferred examples are acrylic and methacrylic acid esters, such as diglycerol diacrylate, polyethyleneglycol dimethacrylate, acrylates and methacrylates of trimethylol ethane, trimethylol propane and pentaerythritol and polyhydric alicyclic alcohols. Reaction products of diisocyanates with partial esters of polyhydric alcohols are also used advantageously. Monomers of this kind are described in DE-A Nos. 20 64 079, 23 61 041 and 28 22 190.

The proportion of monomers contained in the layer in general varies between 10 and 80, preferably 20 and 60, percent by weight.

A great number of soluble organic polymers may be employed as binders. Examples are: Polyamides, polyvinyl esters, polyvinyl acetals, polyvinyl ethers, epoxide resins, polyacrylic acid esters, polymethacrylic acid esters, polyesters, alkyd resins, polyacrylamide, polyvinyl alcohol, polyethylene oxide, polydimethyl acrylamide, polyvinyl pyrrolidone, polyvinylmethyl formamide, polyvi-

nylmethyl acetamide and copolymers of the monomers which form the homopolymers enumerated.

Other possible binders are natural substances or modified natural substances, for example gelatin and cellulose ethers.

With particular advantage, those binders are used which are insoluble in water, but soluble or at least swellable in aqueous-alkaline solutions, since layers containing such binders can be developed with the preferably employed aqueous-alkaline developers. Binders of this type can, for example, contain the following groups: $-\text{COOH}$, $-\text{PO}_3\text{H}_2$, $-\text{SO}_3\text{H}$, $-\text{SO}_2\text{NH}-$, or $-\text{SO}_2-\text{NH}-\text{CO}-$.

Examples of these are: maleate resins, polymers of β -methacryloyloxy-ethyl N-(p-tolyl-sulfonyl)-carbamate and copolymers of these and similar monomers with other monomers, and also styrene/maleic acid anhydride copolymers. Copolymers of alkylmethacrylate and methacrylic acid and copolymers of methacrylic acid, alkylmethacrylates and methylmethacrylate and/or styrene, acrylonitrile, and the like, which are described in DE-A 20 64 080 and DE-A 23 63 806, are preferably used.

In general, the quantity of binder amounts to 20 to 90, preferably 40 to 80, percent by weight of the layer constituents.

Depending on their intended use and desired properties, the photopolymerizable mixtures may contain various additional substances. Examples of such admixtures are:

- inhibitors to prevent thermal polymerization of the monomers,
- hydrogen donors,
- substances regulating the sensitometric properties of layers of this type,
- dyes,
- colored and uncolored pigments,
- color formers,
- indicators,
- plasticizers, a.s.o.

These constituents advantageously should be selected such that their absorption in the range of actinic radiation which is important for the initiation process is as low as possible.

Within the scope of this invention, actinic radiation is to be understood as any radiation, the energy of which corresponds at least to that of shortwave visible light. Longwave UV-radiation, but also electron radiation, X-rays and laser radiation are suitable.

The photopolymerizable mixture of this invention can be used in many fields of application, such as, for example, the production of safety glass, varnishes which

are hardened by the action of light or corpuscular radiation, such as electron beams, dental fillings and, in particular, as a light-sensitive copying material in the field of reproduction.

The detailed description of the invention is restricted to this last field of application, but without the invention being limited thereto. Examples of possible applications in this field are: copying layers for the photomechanical production of printing forms suitable for relief printing, lithographic printing, gravure printing, screen printing, of relief copies, for example, in the production of Braille books, of single copies, tanned images, pigment images, a.s.o. The mixtures may further be employed for the photomechanical production of etch resists, for example for name plates, printed circuits and chemical milling. The mixtures of this invention are of particular importance with regard to the photomechanical production of lithographic printing forms and etch resists, especially in the form of presensitized materials.

The mixture can be used industrially for the above mentioned applications as a liquid solution or dispersion, for example, a photoresist solution, which is applied by the consumer to an appropriate support, for example, for chemical milling, for the production of printed circuits, screen printing stencils, a.s.o. The mixture may also be present as a solid light-sensitive layer on a suitable support, i.e., as a storable, presen-

sitized copying material, for example, for the production of printing forms. It can also be employed for the production of dry resists.

It is in general advantageous to substantially isolate the mixtures from the influence of atmospheric oxygen during the light polymerization. If the mixture is used in the form of thin copying layers, it is recommended to apply a suitable cover film which has a low permeability to oxygen. The cover film may be self-supporting and be peeled off from the copying layer prior to development. Polyester films, for example, are suitable for this purpose. The cover film may also consist of a material which dissolves in the developer liquid or which can be removed at least from the non-hardened areas during development. Examples of materials suitable for this purpose are, inter alia, waxes, polyvinyl alcohol, polyphosphates, sugars, a.s.o.

Layer supports which are suitable for copying materials prepared using the mixture of this invention include, for example, aluminum, steel, zinc, copper and plastic films, such as films of polyethylene terephthalate or cellulose acetate, and screen printing supports, such as perlon gauze.

The light-sensitive materials employing the mixture of this invention are prepared in known manner. Thus, the mixture can be taken up in a solvent, and the resulting solution or dispersion can be applied to the intended

(19)

support as a thin film by casting, spraying, immersion or by roller application and subsequently dried. Thick layers (for example, of 250/ μ m and thicker) are advantageously prepared by first producing a self-supporting film by extrusion or molding, which is then laminated to the support. In the case of dry resists, solutions of the mixture are applied to transparent supports and dried. The light-sensitive layers - thickness between about 10 and 100/ μ m - are then also bonded to the desired substrate by lamination together with the temporary support.

The copying materials are processed in known manner. They are developed by treatment with an appropriate developer solution, preferably a weakly alkaline aqueous solution, whereby the unexposed areas of the layer are dissolved away and the exposed areas of the copying layer remain on the support.

The following text gives examples of the mixture of the present invention. First, the production of a number of novel photoinitiators according to the invention is described.

In the production prescriptions and the Examples which follow, parts by weight (p.b.w.) and parts by volume (p.b.v.) bear the same relationship as the g and the cm^3 . Unless otherwise stated, percentages and quantities are to be understood as weight units.

(20)

Most of the initiators contained in the mixture of this invention are not known from prior publications. They are prepared in accordance with the following general procedure:

A) General procedure for preparing the compounds I:

1 mole of 2,4-6-trichloropyrimidine-5-carbaldehyde is reacted with 1 mole of arylthiol and 1.1 moles of triethyl amine, in tetrahydrofuran, at temperatures of -50 to -30°C; then the amine hydrochloride is separated off by filtration, and the residue left after removing the solvent by distillation is crystallized by mixing with an appropriate solvent. The 2,4-dichloro-6-arylthiopyrimidine-5-carbaldehydes (compounds 1 to 31) thus obtained decompose in the solid state and are immediately further processed. Therefore, the figures in Table 1 denote the raw yields.

- 13 -

Table I

Compounds of the formula I:

No.	R ¹	R ²	R ³	R ⁴	Yield %
1	H	H	H	H	71.9
2	H	H	H	CH ₃	34.8
3	H	H	CH ₃	H	52.5
4	H	CH ₃	H	H	63.8
5	H	F	H	H	56.1
6	H	H	H	Cl	54.1
7	H	H	Cl	H	56.1
8	H	Cl	H	H	40.7
9	H	Br	H	H	69.1
10	H	H	H	OCH ₃	66.0
11	H	H	H	COOH	75.9
12	H	H	H	COOCH ₃	61.0
13	H	COOH	H	H	31.3
14	H	H	CH ₃	CH ₃	25.5
15	H	CH ₃	H	CH ₃	57.5
16	CH ₃	H	H	CH ₃	56.8
17	H	H	Cl	CH ₃	72.2
18	H	Cl	H	CH ₃	65.9
19	Cl	H	H	CH ₃	67.7
20	H	H	CH ₃	Cl	82.1
21	H	CH ₃	H	Cl	66.9
22	H	H	Cl	Cl	39.1
23	Cl	H	H	Cl	67.6
24	Cl	H	Cl	H	71.7
25	CH ₃	CH ₃	H	CH ₃	45.2
26	CH ₃	Cl	H	CH ₃	57.5
27	CH ₃	Cl	H	Cl	56.8
28	H	Cl	Cl	Cl	53.7
29	Cl	Cl	H	Cl	33.5
30	H	H	- benzo -		40.1
31	- benzo -		H	H	76.1

General procedure used for preparing the compounds of formula II:

1 p.b.w. of one of the compounds 1 to 31 is stirred in 20 p.b.w. of H_2SO_4 (98 %) at a temperature of $70^\circ C$, the mixture is heated to 110 to $150^\circ C$ until the formation of HCl is completed, poured onto 120 p.b.w. of ice, adjusted to a pH of 4 at temperatures of $30^\circ C$ to $40^\circ C$ by means of an alkali compound, the solids are separated off, dried and recrystallized from dimethyl formamide.

Table 2

1,3-diaza-9-thia-anthracene-2,4-diones of the formula II:

No.	R ¹	R ²	R ³	R ⁴	Melting Point $^\circ C$	Yield %
32	H	H	H	H	290	62.3
33	H	H	CH ₃	H	300	68.4
34	H	H	H	CH ₃	300	64.8
35	H	F	H	H	280	11.5
36	H	Cl	H	H	300	17.6
37	H	H	H	Cl	290	50.7
38	H	Br	H	H	280	10.5
39	H	H	H	COOH	280	21.6
40	H	H	H	COOCH ₃	270	5.2
41	CH ₃	H	H	CH ₃	270	22.2
42	H	CH ₃	H	CH ₃	310	6.6

Continuation Table 2

No.	R ¹	R ²	R ³	R ⁴	Melting Point °C	Yield %
43	H	H	CH ₃	CH ₃	270	6.8
44	Cl	H	H	CH ₃	290	52.7
45	H	Cl	H	CH ₃	300	35.9
46	H	CH ₃	H	Cl	290	47.8
47	Cl	H	Cl	H	210	42.3
48	Cl	H	H	Cl	270	49.7
49	CH ₃	CH ₃	H	CH ₃	300	9.7
50	CH ₃	Cl	H	CH ₃	350	54.0
51	CH ₃	Cl	H	Cl	280	11.2
52	Cl	Cl	H	Cl	280	3.2
53	- benzo -		H	H	300	42.8
54	H	H	- benzo -		290	42.8

The initiating activity of the compounds nos. 32 to 54 is compiled in the Examples which follow and the accompanying tables.

Example 1

A solution of

4.0 p.b.w. of a methylmethacrylate/methacrylic acid copolymer (acid number about 110)

4.0 p.b.w. of trimethylolethanetriacrylate,

0.08 p.b.w. of a blue azo dyestuff obtained by coupling

2,4-dinitro-6-chlorobenzene diazonium salt
with 2-methoxy-5-acetylamino-N-cyanoethyl-N-
hydroxyethylaniline, and

0.21 p.b.w. of initiator, in
38 p.b.w. of ethyleneglycol monoethyl ether and
18 p.b.w. of butyl acetate

is spin-coated onto electrolytically grained and anodi-
cally oxidized, 0.3 mm thick aluminum and dried, in a way
such that a dry layer weight of 25 g/m² is obtained.

After drying, the photopolymer layer is provided with
a coating comprised of a solution of

5 p.b.w. of polyvinyl alcohol (12 % residual acetyl
groups, K-value 8), in
95 p.b.w. of purified water

and dried, so that a peelable cover layer having a weight
of about 5 g/m² is obtained.

Subsequently, the plate is exposed for 40 seconds by
means of a 5 kW metal halide lamp, through a 13-step
exposure wedge. After exposure, the plate is heated to
120°C for 1 minute. Then the exposed photopolymer
layer is developed for about 1 minute with a developer of

1.5 p.b.w. of sodium metasilicate x 9 H₂O
0.01 p.b.w. of a polyoxyethylene ether of coconut fatty
alcohol having about 8 oxyethylene units, and

98.3 p.b.w. of purified water,

using a cotton pad.

The plate is rinsed with water and rendered acidic with 1 % strength phosphoric acid and inked with a greasy ink.

After inking, the plate is treated with a commercially available desensitizing gumming solution and dried. On an offset press about 100,000 prints can be run.

The following light sensitivities are measured:

<u>Compound</u>	<u>Developed solid steps</u>
32	2
33	3
34	2
35	1
36	1
37	5
38	2
39	3
40	2
41	2
42	1
43	2 - 3
44	4
45	4
46	4
47	2 - 3
48	5

<u>Compound</u>	<u>Developed solid steps</u>
49	2
50	2
51	1
52	2
53	1
<u>54</u>	<u>2 - 3</u>

Example 2

7 solutions, which are each composed of

- 5.6 p.b.w. of the product obtained by reacting 1 mole of 2,2,4-trimethyl-hexamethylene diisocyanate with 2 moles of 2-hydroxy-ethyl methacrylate,
- 6.5. p.b.w. of a terpolymer of styrene, n-hexyl-methacrylate and methacrylic acid (10:60:30),
- 0.2 p.b.w. of one of the compounds 33,37,39,44,45,46 and 48
- 0.15 p.b.w. of triethylene glycol dimethacrylate, and
- 0.035 p.b.w. of the blue azo dyestuff described in Example 1, in
- 30 p.b.w. of butanone and
- 0.5 p.b.w. of ethyl alcohol

are successively spin-coated onto 25 μm thick polyethylene terephthalate film, in a way such that a 25 μm thick layer (30 g/m^2) is obtained. Then drying is per-

- 19 -

formed in a drying cabinet at 100°C for 2 minutes.

In order to protect the layers thus produced from damage and contamination by dust, they are covered with a cover film of a thickness of 20-25 μm , which adheres less strongly to the layer than the polyester film. Having been thusly treated, they can be stored over a relatively long period of time.

The copper surface of a phenoplast laminate plate, to which a 35 μm thick copper foil is bonded, is mechanically cleaned with pumice powder or a brushing machine and blown dry with oil-free air after thorough rinsing with water.

The cover film is peeled off, and the dry resist is laminated onto the cleaned copper plates by means of a laminating device equipped with heated rolls, at a temperature of 120°C and a speed of 1.5 m/min.

Then the seven samples are exposed through the support film, under a 13-step exposure wedge having density increments of 0.15. Exposure is performed by means of a 5 kW metal halide lamp, the exposure times are 10, 20 and 40 seconds.

The wedge step 0 corresponds to an optical density of 0.05 (auto-absorption of the film material).

After removal of the support film, the plates are spray-developed with an 0.8 % sodium carbonate solution. The developing time is about 60 seconds at a temperature of 23°C.

In order to test the resistance to overdevelopment - a test to find out whether the wedge steps are completely cross-linked - the samples are subjected to the threefold developing time, i.e., 180 seconds, after exposure for 20 seconds.

In the following table, the completely cross-linked wedge steps of the dry resist layers are compiled, the layers differing from one another merely by the photoinitiator used in each case:

Compound	Solid steps in the sprayer at			Solid steps at 180 sec. development
	10 sec	20 sec	40 sec	
	exposure			
33	-	1	3	-
37	2	4	6	3
39	-	1	3	-
44	1	3	5	2
45	1	3	5	2
46	1	3	5	2
48	2	4	6	3

Example 3

0.4 g of each of the compounds 37 and 48 are added to photopolymer mixtures, as described in Example 2, and the solutions are spin-coated onto 25 μ m thick polyethylene terephthalate films, in a way such that 25 μ m thick layers (30 g/m²) are obtained.

Following the procedure of Example 2, the layers are then applied to the cleaned copper surfaces of Cu-phenolic resin laminate plates having a size of 10 cm x 15 cm each, exposed through the support film and developed with an 0.8 % aqueous sodium carbonate solution.

The following numbers of completely cross-linked wedge steps result (comparison: solid steps when 0.6 g of initiator is added in each case):

com- pound	Solid steps with 0.4 g of initiator Exposure time (sec)			Comparison: Solid steps with 0.6 g of initiator Exposure time (sec)		
	10	20	40	10	20	40
37	3	6	8	2	3	5
48	3	5	7	2	4	6

(30)

- 22 -

Example 4

A solution of

- 1.0 p.b.w. of trimethylolethane triacrylate,
- 1,4 p.b.w. of a terpolymer obtained from n-hexyl methacrylate, methyl methacrylate and methacrylic acid (50:25:25) and having an acid number of about 160,
- 0.02 p.b.w. of Sudan Blue II, and
- 0.05 p.b.w. of compound 37, in
- 6.0 p.b.w. of butanone

is spin-coated onto a cleaned single-stage zinc etch plate and dried, in a way such that a layer weight of about 10 g/m² is obtained.

Thereafter, the copying material is provided with a 1-2 μ m thick coating of polyvinyl alcohol, dried and exposed for 40 seconds under a positive original using a 5 kW metal halide lamp. The zinc plate is developed for 45 seconds with a developer composed of

- 1.5 p.b.w. of sodium metasilicate nonahydrate
- 0.3 p.b.w. of polyglycol 6,000
- 0.3 p.b.w. of levulinic acid and
- 97.6 p.b.w. of purified water.

After thorough rinsing with water, etching is performed for 5 minutes with 10 % strength nitric acid con-

taining an edge protecting agent. The hardened photopolymer layer is removed with ethyleneglycol monobutyl ether. The printing form obtained can be used for high quality book printing.

Example 5

A coating solution as described in Example 4, but containing 0.05 p.b.w. of compound 48 instead of compound 37 is applied by casting to a 25 μm thick polyethylene terephthalate film, in a way such that a 20 μm thick layer (26 g/m^2) is obtained. Then drying is performed at 100°C in a drying cabinet for 2 minutes.

Together with the polyester film, the dried layer is laminated onto a screen printing cloth VS Monoprint P 77 made by Verseidag, Krefeld, by means of a laminating device employing maximum pressure, a temperature of 115°C, and a speed of 1 m/min.

Thereafter, exposure is performed under a positive original for 60 seconds through the polyester film, by means of a 5 kW metal halide lamp.

The polyester film is removed and the non-crosslinked image areas are removed with the developer described in Example 4 in a swing bath within 45 seconds. After thorough rinsing with water and drying the screen printing form is ready for use.



0 102 586

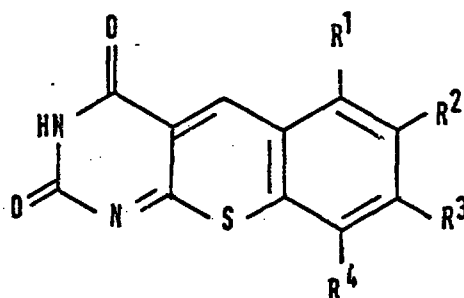
(32)

- 24 -

Claims:

1. A photopolymerizable mixture which contains, as essential components,

- a) a polymeric binder
- b) a polymerizable compound having at least two terminal ethylenically unsaturated groups and a boiling point of more than 100°C, and
- c) a polynuclear N-heterocyclic compound as a photoinitiator, characterized in that the N-heterocyclic compound has the general formula II



(II)

wherein

R^1 , R^2 , R^3 and R^4 are identical or different and individually each denote a hydrogen or halogen atom, a carboxy group, an alkyl, alkoxy or alkoxy-carbonyl group in which each alkyl group has from 1 to 6 carbon atoms, or a combination of two of them each denotes a fused aromatic radical.

2. Photopolymerizable mixture as claimed in Claim 1, characterized in that it contains a compound of the formula II wherein one of the radicals R^1 to R^4 is a hydrogen atom.



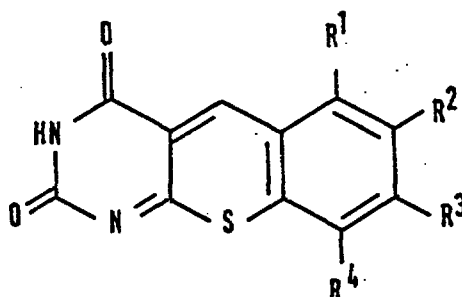
0 102 536

33

- 25 -

3. Photopolymerizable mixture as claimed in Claim 2, characterized in that it contains a compound of the formula II wherein two or three of the radicals R^1 to R^3 are hydrogen atoms.

4. 1,3-diaza-9-thia-anthracene-2,4-diones of the general formula (II)



(II)

wherein

R^1 , R^3
and R^4

are identical or different and individually each denote a hydrogen or halogen atom, a carboxy group, an alkyl, alkoxy or alkoxy-carbonyl group in which each alkyl group has from 1 to 6 carbon atoms, and

R^2

denotes a carboxyl, an alkoxy or alkoxy-carbonyl group, in which each alkoxy group has from 1 to 6 carbon atoms, or a combination of two of the radicals

R^1 , R^2 , R^3
and R^4

each denotes a fused aromatic radical.