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3,671,252

PHOTOSENSITIVE CYCLIC POLYIMIDES COMPOSITION

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Int. Cl. G03c 1/52
U.S. Cl. 96—90 5 Claims

ABSTRACT OF THE DISCLOSURE

A photographic material free from silver halide containing cyclic polyimides as photosensitive compounds which are converted into dark-coloured substances under the effect of light. An image formed during exposure of the recording material according to the invention can be erased spontaneously or by additional specific measures so that the material can be re-used.

This invention relates to photosensitive materials containing, as photosensitive additive, cyclic polyimides which are converted into dark-coloured substances under the effect of light.

There are numerous processes in which photosensitive organic substances are used for image recording. Some of these processes are based on photochemical rearrangements or reactions of organic compounds producing a change in colour. Photochemical reactions of this kind involving organic compouds are comprehensively described in, for example, "Präparative organische Photochemie" (A. Schönberg, Springer Varlag, 1958) and "Light-Sensitive Systems" (J. Kosar, John Wiley & Sons, New York, 1965).

Reactions of this kind include, for example, the formation of monomethine dyes during the photolysis of trihalogenomethyl compounds in ultra-violet light in the presence of aromatic or heterocyclic compounds of the kind which, by virtue of their constitution, contain OH ring members that are particularly reactive for condensation and diazo coupling.

In these processes, either the layers are photosensitive from the outset or, alternatively, the reaction components of the photochemical reaction have to be added before exposure.

Conventional systems are limited in their practical application because their photosensitivity is generally inadequate.

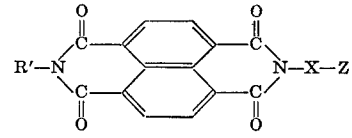
The photosensitive materials described in French patent specification No. 1,526,496 provide some improvement. These materials contain cyclic imides of aryl polycarboxylic acids whose imide nitrogen is substituted by olefinically unsaturated aliphatic or cycloaliphatic groups.

The photosensitivity of these substances also, does not completely satisfy practical requirements. In addition, they cannot be used for special recording materials of the kind required for computers and oscillographs, which are not only required to have a relatively high sensitivity to light, but in which the image-forming reaction is also intended to be reversible. In other words, the image formed is intended to be eradicable so that the recording materials can be re-used.

An object of the present invention is to provide photosensitive materials free from silver halide which show an adequate degree of sensitivity to light and which yield sufficiently dark-coloured reaction products.

Another object of the invention is to provide photographic recording materials in which the image formed during exposure can be erased spontaneously or by additional specific measures so that the material can be re-used.

It has now been found that photographic materials containing cyclic polyimides of the following formula as photosensitive compounds are particularly suitable for recording images:



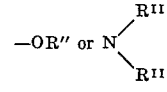
In this formula, R' represents

(1) a group of the formula —X—Z
(2) a hydrogen atom,
(3) a saturated or olefinically unsaturated aliphatic group, with preferably up to 18 carbon atoms, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, dodecyl or allyl, butenyl or pentenyl,
(4) a saturated or unsaturated cycloaliphatic radical such as cyclopentyl, cyclopentenyl, cyclohexyl or cyclohexenyl,
(5) a dihydropyran radical;
the aforementined cyclic radicals can be attached to the nitrogen atom either directly or indirectly through an alkylene bridge, or
(6) a radical containing a 5- or 6-membered ring and a cyclopropane ring preferably with in addition an endomethylene grouping, for example a radical of the tricyclene series, such as tricyclene or nortricyclene:

X represents

(1) a straight or branched saturated or olefinically unsaturated aliphatic chain, with preferably up to 5 carbon atoms, which can be interrupted by hetero atoms such as oxygen, sulphur or the group $>NR^{II}$, phenylene rings or cycloaliphatic rings,
(2) a saturated or unsaturated cycloaliphatic radical such as cyclopentylene or cyclohexylene or,
(3) a single chemical bond;

Z represents



or nitrile,

R^{II} represents hydrogen or a saturated or olefinically unsaturated aliphatic group with preferably up to 5 carbon atoms, especially methyl, or cycloalkyl, for example cyclopentyl or cyclohexyl,

R^{III} represents the aliphatic saturated or olefinically unsaturated group with preferably up to 5 carbon atoms, especially methyl, or cycloalkyl such as cyclopentyl or cyclohexyl, or

R^{II} and R^{III} together with the nitrogen atoms to which they are attached represent a saturated heterocyclic ring optionally containing a further hetero atom or atoms, especially one of the following rings: azacyclopropane, pyrrolidine, morpholine, thiomorpholine, piperidine or piperazine; these rings can contain a keto group, as in the cyclic carboxylic acid imides.

The compounds described in the foregoing become dark-coloured very quickly on exposure to light, especially ultraviolet light, and, in doing so, very simply yield photographic images if they are dispersed in a binder layer, in a completely dry process.

The following compounds for example are suitable:

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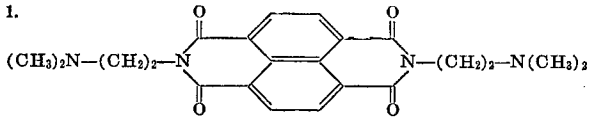

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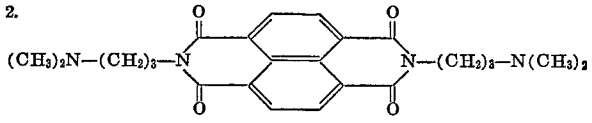

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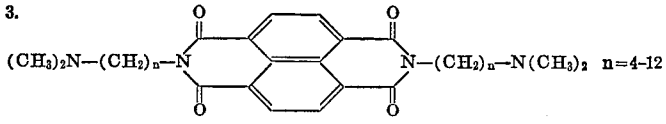

n=4-12

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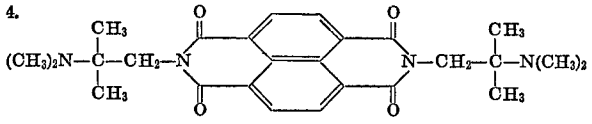

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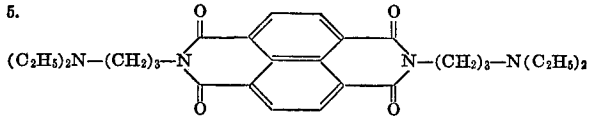

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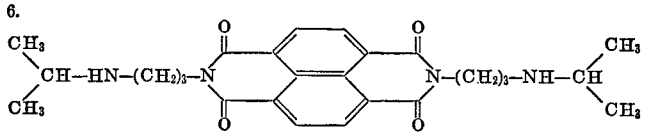

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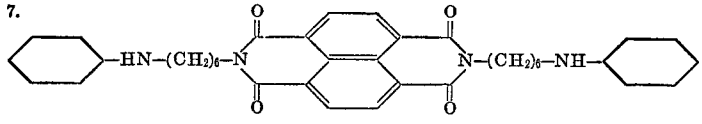

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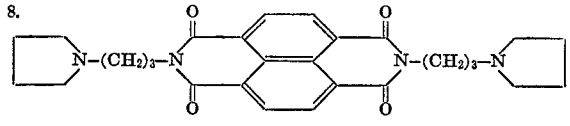

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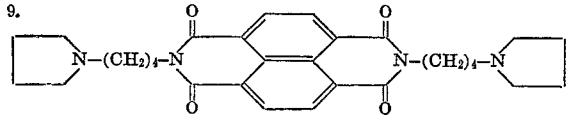

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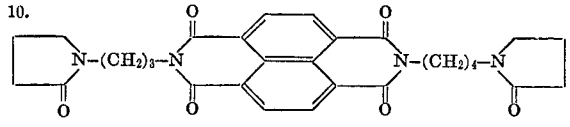

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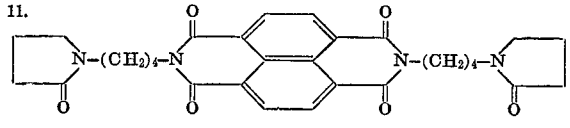

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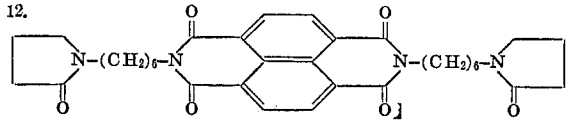

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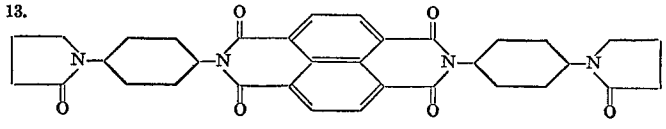

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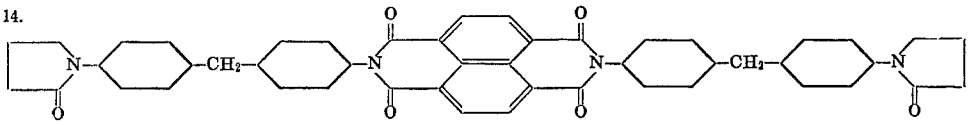

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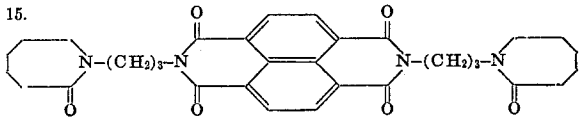

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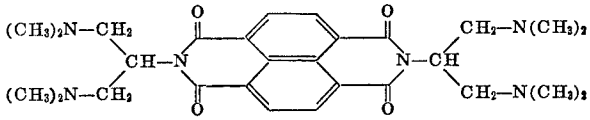

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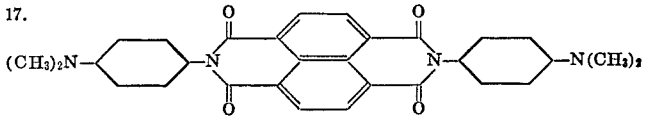

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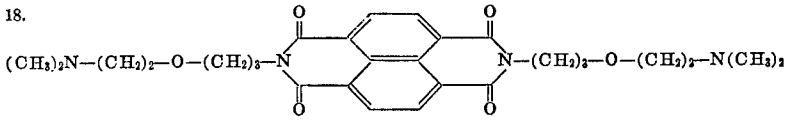

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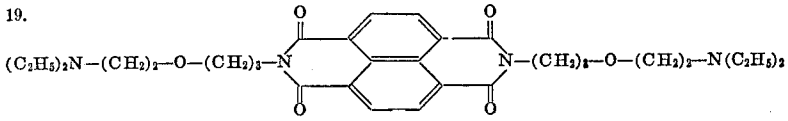

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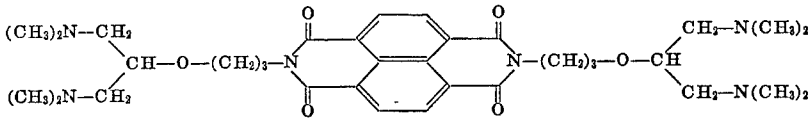

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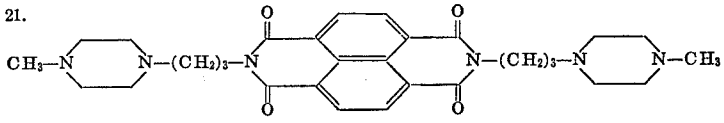

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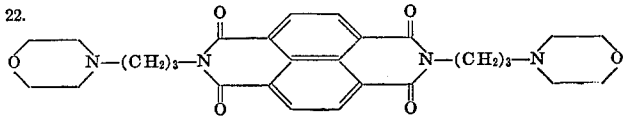

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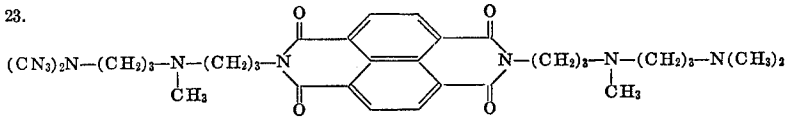

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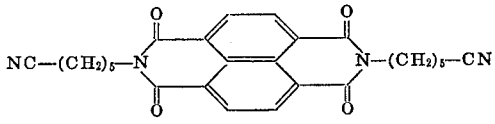

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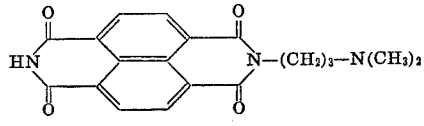

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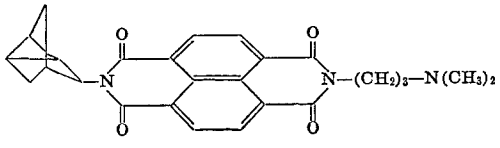

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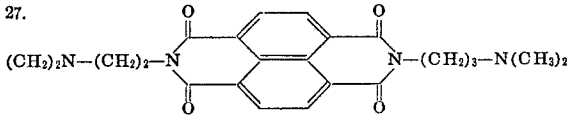

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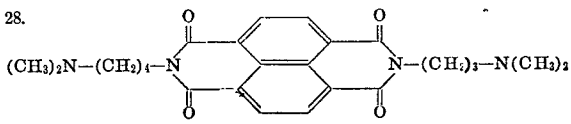

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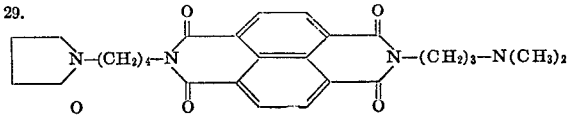

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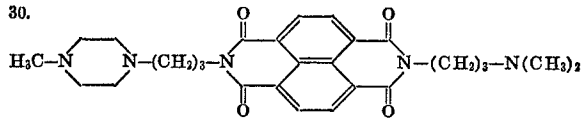

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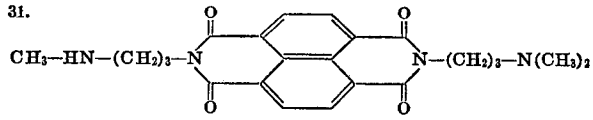

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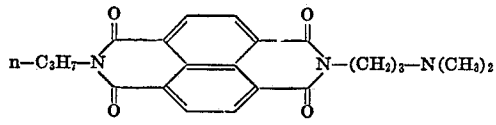

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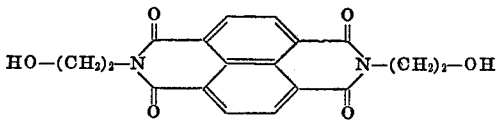

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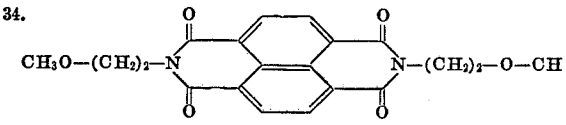

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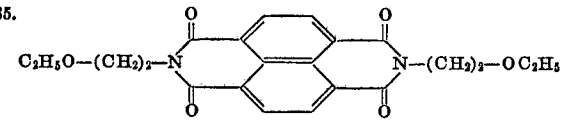

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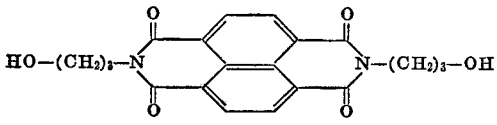

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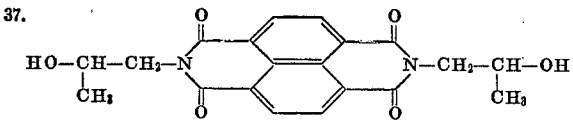

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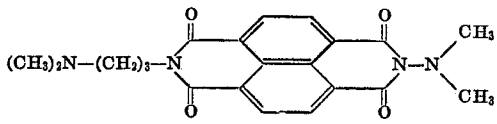


The compounds used in accordance with the invention can be obtained by various known processes, for example by reacting naphthalene-1,4,5,8-tetracarboxylic acid dianhydride or naphthalene-1,4,5,8-tetracarboxylic acid with the corresponding amines in the presence of a suitable solvent or in the melt. Examples of suitable solvents include ethanol, dimethyl formamide or N-methyl pyrrolidone which absorb the water formed during the reaction. It is also possible with equal effect to use toluene or xylene as solvents by which the water formed during the reaction can be readily removed at the boiling temperature through azeotropic distillation in a water separator. The preparation of basic alkylated naphthalene-1,4,5,8-tetracarboxylic acid diimides is described for example in German patent specification No. 1,195,762.

The preparation of a few representative compounds is described in detail below. The others are similarly prepared.

COMPOUND 2

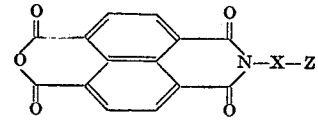
10.2 parts by weight of 3-amino-1-dimethylamino propane are dissolved in 150 parts by weight of dimethyl formamide. 13.4 parts by weight of naphthalene-1,4,5,8-tetracarboxylic acid dianhydride are introduced in portions into the solution at room temperature, producing a rise in temperature from 25° C. to 35° C. The mixture is

then heated under reflux for 2 hours. After cooling, the reaction mixture is filtered and the residue is washed with alcohol. 19.5 parts by weight of a light yellow crystalline compound of Formula 2, having a melting point of from 226 to 228° C. are obtained. The infra-red spectrum and elemental analysis confirm the assumed structure.

COMPOUND 11

As in the preparation of Compound 2, 15.6 parts by weight of N-(4-aminobutyl-pyrrolidone in 150 parts by volume of ethanol are reacted with 13.4 parts by weight of naphthalene-1,4,5,8-tetracarboxylic acid dianhydride to form the diimide. The reaction product is obtained in the form of colourless crystals melting at 217° C. in a yield of 24.2 parts by weight.

Asymmetrically substituted naphthalene-1,4,5,8-tetracarboxylic acid diimides are obtained by initially preparing a mixed-anhydride-imide (stage A)

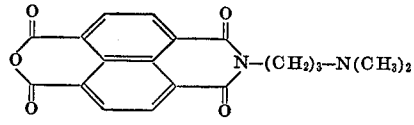


(stage A)

and then reacting it with a second correspondingly substituted amine to form the asymmetrically substituted imide. Stage A can be prepared for example by reacting naphthalene-1,4,5,8-tetracarboxylic acid dianhydride with a quantity of an amine corresponding to only one anhydride group in a suitable solvent. This is followed, either after isolation of stage A or even in a one-stage process, by reaction with the corresponding quantity of a second amine different from the first to form the asymmetrically substituted imide. The preparation of a few representative compounds is described in detail in the following. The others are similarly prepared.

PREPARATION OF COMPOUND 26

Stage A: 26.8 parts by weight of naphthalene-1,4,5,8-tetracarboxylic acid dianhydride are dissolved under heat in 900 parts by volume of dimethyl formamide, followed by the dropwise addition at the reflux temperature of 10.2 parts by weight of 3-amino-1-dimethylamino propane. This is followed by stirring for 2 hours under reflux. After cooling, the mixture is filtered and the residue is washed with 120 parts by volume of alcohol. The asymmetrical compound melting at 295° C. is obtained in a yield of 18.70 parts by weight.



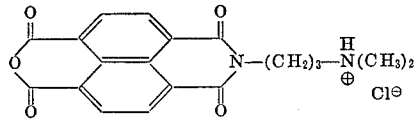
The infra-red spectrum and elementary analysis (N_{theory} =7.96%, N_{found}=7.9%) confirm the assumed structure. The substance is weakly sensitive to light.

17.6 parts by weight of the above-identified compound (Stage A) are reacted in 150 parts by volume of dimethyl formamide with 5.45 parts by weight of nortricyclylamine and heated under reflux for 4 hours. After cooling, the mixture is filtered and the filter residue washed with alcohol. A very pale yellow crystalline compound of Formula 26 with a melting point of 237–239° C. is obtained in a yield of 18.2 parts by weight, its structure being confirmed by the infra-red spectrum.

COMPOUND 30

Stage A: 30.4 parts by weight of naphthalene-1,4,5,8-tetracarboxylic acid are dissolved under heat in a solution of 200 parts by weight of crystalline sodium acetate and 900 parts by volume of water, followed by the dropwise addition of 10.2 parts by weight of 3-amino-1-dimethylamino propane over a period of 15 minutes at 75° C. This is followed by stirring for 10 hours at 75° C. After cooling, the reaction mixture is filtered off from a

slight sediment, strongly acidified with concentration hydrochloric acid and boiled for 20 minutes. After cooling with ice, it is filtered and the residue is washed with alcohol and dried. The compound



melting at 28° C. is obtained in a yield of 31.6 parts by weight.

15.7 parts by weight of N-methyl-N'-3-aminopropylpiperazine are added dropwise at room temperature to 19.4 parts by weight of the above identified compound dissolved in 150 parts by volume of dimethyl formamide, producing a rise in temperature from 28 to 48° C. This is followed by heating for 4 hours under reflux, resulting in precipitation. After cooling, the product is filtered off, the residue washed with 80 parts by volume of alcohol and then dried. A pale yellow crystalline compound of Formula 30 melting at 210 to 213° C. is isolated in a yield of 24.3 parts by weight, its structure being confirmed by the infra-red spectrum and elemental analysis.

The photochemical reaction of the aforementioned compounds proceeds both in solution and also in the solid phase. When the reaction is carried out in practice, these substances are applied to any type of layer support either individually or in the form of mixtures of several photosensitive polyimides, in solution or in fine disperison, with or without binders. Positive images are then obtained by ultra-violet irradiation under a negative line or continuous tone original. The substances are applied by conventional methods, including spreading or spraying solutions or by casting from solutions or suspensions of layer-forming natural colloids or plastics, for example gelatine, cellulose, celluose esters, cellulose ethers, polycarbonates (especially those based on bis-phenylol alkanes) polyesters (especially tohse based on polyethylene terephthalate), polyamides, polyurethanes and a variety of film-forming polymers or copolymers of olefinically unsaturated monomers such as vinyl chloride, vinyl acetate or styrene, olefinically unsaturated carboxylic acids, their esters or other derivatives, for example maleic acid anhydride, acrylic acid or methacrylic acid and their derivatives, also polyethylene or polyvinylidene chloride, for example in the form of their aqueous dispersions.

The compounds to be used in accordance with the invention can also be dissolved in aqueous media. By the addition of acids, the substances containing basic nitrogen atoms are made soluble through salt formation.

After the diimides have been dissolved in the aqueous binder solution, the diimides can be precipitated again in fine dispersion by increasing the pH value. The photosensitivity of the free amines is considerably higher than that of the salts.

The concentration of the photosensitive substances in the binder can be varied within any limits. Gradation and maximum density can be influenced by varying both the concentration and the quantity applied. When binders swellable in water, such as gelatin for example, are used, the pH value can be varied within limits inside which the binder does not undergo any excessive change, for example degradation in the case of gelatin. The substances are preferably used in quantities of from 1 to 80%, based on the dry layer. UV-containing light sources are particularly, suitable for exposure, although direct daylight and sunlight and also mercury vapour lamps are also suitable.

The photosensitive compounds used in accordance with the invention can also be used in self-supporting layers for which purpose layer binders of the aforementioned kind are also suitable. In principle, the nature of the layer binder is by no means critical and can be selected without any problems from the large number of conventional natural or synthetic hydrophilic or hydrophobic layer-forming binders by simple preliminary tests.

When exposed to light, the photosensitive compounds used in materials according to the invention yield coloured products which, when stored in the dark, are converted back into the colourless starting compounds more or less quickly (periods of from a few minutes to a few days are required).

Return of the coloured image substance to the colourless photosensitive starting form can be accelerated to a considerable extent by heating. If the material containing the image is heated at a temperature of from 60 to 100° C., and preferably at a temperature of from 80 to 100° C., the image disappears in a few seconds. The photosensitive material remains completely usable and can immediately be re-exposed. With layers of this kind, it is possible to erase any desired particular part of the image by controlled image-wise infra-red irradiation of the image.

For these reasons, the materials according to the invention are of particular significance to processes of the kind in which it is required to erase the image and re-use the material.

It is possible to fix the photographic images thus obtained by rendering the still unexposed portion of the cyclic polyimides insensitive to light. This can be done for example by the action of reagents which react with unsaturated double bonds or have a cleaving effect upon cyclopropane rings for example. Suitable reagents reacting with unsaturated double bonds include inter alia halogens such as bromine, chlorine or iodine, hydrohalic acids such as hydrogen chloride or hydrogen bromide, ozone, peroxy acids or hydrogen, sulphenyl chlorides, sulphur dichloride, or potassium permanganate. Another method of converting the photosensitive polyimides into compounds which are not sensitive to light is to detach the imide group, for example by hydrolysis, to give a polyamido carboxylic acid or by aminolysis to give polyamides. Exposed and unexposed portions of the photosensitive cyclic polyimides can also be separated by selectively dissolving out one of the components by means of suitable solvents.

It is also possible to obtain direct positive images which are stable in daylight by using the photographic materials according to the invention. One suitable process is described in copending U.S. patent application Ser. No. 85,811 filed Oct. 30, 1970. In this process, the material exposed to form an image is heated to a temperature of about 100 to 200° C. The coloured, radical substance formed over the exposed areas is converted irreversibly into colourless or substantially colourless products. The photosensitive cyclic polyimide in those parts of the layer which have remained unexposed is in no way affected by the heating. Those parts of the layer which were not exposed during image-wise exposure are made dark in colour through a uniform after-treatment with actinic light, especially ultra-violet light, whilst the original areas exposed to form an image remain light. Accordingly, a reversal image which is stable in daylight is obtained.

By adopting the procedure which has just been described, it is possible to obtain offset foils which can be processed dry from the materials according to the invention. By heating the material exposed to form an image to a temperature of about 100 to 200° C., followed by uniform exposure with ultra-violet light, the physical properties of the layer are altered image-wise. This is externally apparent from the fact that, following after-exposure with ultra-violet light, those areas exposed image-wise are extremely glossy whilst the remaining portions of the image are matte in appearance. In addition, the wetting properties have also been modified in so far as the glossy image-wise exposed areas have become hydrophobic and readily absorb fatty printing inks. The remaining areas of the layer are hydrophilic and repel printing inks. The images produced in accordance with this embodiment can therefore be used immediately as blocks for offset printing processes.

It is possible by additional measures further to increase the differences in wettability. For example, the photosensitive substances can be applied, with or without layer binders, to a highly hydrophilic layer support, such as a suitably coated paper. After heating and exposure with ultra-violet light, it is readily possible to remove the already somewhat hydrophilic portions of the layer by rubbing briefly with a damp cloth or sponge, thus exposing the highly hydrophilic surface of the layer support. Surprisingly, those areas of the layer exposed to form an image adhere much better to the support so that they cannot be removed by rubbing. These effects can be enhanced as required by suitably modifying the photosensitive layers. The offset foils thus obtained can be employed in the usual way in offset printing processes.

Instead of the photosensitive cyclic polyimides described above it is also possible to use in the layers open-chain intermediates of these compounds, which intermediates unlike the polyimides are unaffected by light but which can be converted into the photosensitive products of the above forms by a simple, brief treatment, such as heating or even chemical treatment. The intermediates which are not sensitive to light are polyamido polycarboxylic acids.

Example 1

A solution consisting of
4 g. of bis-(2-ethyl-hexyl) succinate,
5 g. of compound 11 dissolved in 75 ml. of methylene chloride and
7 ml. of dibutyl phthalate

is emulsified into a solution of 50 g. of gelatin in 450 ml. of water. The product of emulsification is diluted with 200 ml. of water, followed by the addition of 10 ml. of a 10% by weight aqueous solution of saponin, 0.6 ml. of a 30% by weight aqueous solution of formaldehyde and 10 ml. of a 50% by weight aqueous solution of glycerol.

The product is exposed imagewise with an electronic flash (Braun F. 65 distance 10 cm.). A negative grey image of the original is obtained. Photosensitivity is relatively high, and extends in the spectrum up to around 500 nm.

At room temperature, the image has disappeared almost completely after storage for 2 hours in darkness. If it is heated to a temperature of from about 90 to 120° C. the image disappears completely in 2 to 10 seconds. The image can be removed particularly quickly by the action of hot water vapour (for example at 70° C.).

The layer remains photosensitive and can be re-used.

Example 2

A mixture of 5 g. of compound 1 dissolved in 300 ml. of chloroform and 200 ml. of polyvinyl acetate (20% by weight solution in chloroform) is cast on to a baryta paper support.

It is exposed image-wise (with a mercury vapour lamp arranged at a distance of 35 cm.) with an exposure time of 30 seconds. A negative reddish-brown image is formed which disappears completely on storage for 10 minutes in darkness at room temperature. The image can be removed in 2 to 5 seconds by heating at 90 to 120° C. The material can be used again.

Example 3

4 g. of compound 2 are suspended in 50 ml. of water and the pH is adjusted to a value of 7 with 1 N sulphuric acid as a result of which tht substance is completely dissolved. It is then made up with water to 100 ml. 100 ml. of a 10% by weight aqueous gelatin solution, 5 ml. of a 7.5% by weight aqueous saponin solution and 0.5 ml. of a 30% by weight aqueous formalin solution are added to this mixture. This mixture is cast on to a cellulose triacetate support and dried. Before exposure the layer is briefly exposed to an ammoniacal atomsphere. It is possible in this way to obtain a 5 to 10 fold increase in sensitivity.

The material is exposed as in Example 2 giving a negative brown image of the original (density in white light 0.35, in blue light 0.84) on a transparent support.

Example 4

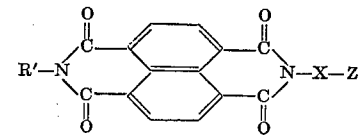
An image prepared in accordance with Example 2 is heated for 3 minutes at 200° C. in a heating chamber. After heating, it is uniformly after-exposed with ultra-violet light or day-light. A reversal image that is relatively stable to light is obtained. These areas exposed image-wise are extremely glossy, whilst the surrounding areas are matte in appearance. The physical change in the layer is irreversible. The image substance of the reversal image disappears on storage for 10 minutes in darkness. The image substance previously present reoccurs reversibly on re-exposure with ultra-violet light or even under the effect of daylight.

A 1% by weight solution of compound 10 in chloroform is cast on to a hydrophilic paper support. This is followed by imagewise exposure with an ultra-violet lamp as described in Example 2. The exposed material is then heated for 2 minutes at 200° C. Following after-exposure with diffused ultra-violet light or even daylight, the image areas are extremely glossy whilst the surroundings are matte in appearance as in Example 4. The binder is completely removed from those areas which have not been exposed image-wise (matte) by gentle rubbing with an alcohol-impregnated pad.

When the resulting material is used as master in an offset printing machine, fatty inks are only absorbed by the relatively hydrophobic areas of the image. Offset prints of high quality are obtained.

We claim:

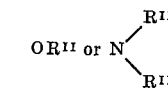
1. A photosensitive photographic material, having as a photosensitive substance a cyclic polyimide of the following formula



wherein R′ represents
(i) a group of the formula —X—Z,
(ii) a hydrogen atom,
(iii) saturated or olefinically unsaturated aliphatic group,
(iv) a saturated or unsaturated cycloaliphatic radical,
(v) a sihydropyran radical,
the above cyclic radicals may be attached to the nitrogen atom either directly or indirectly through alkylene bridge, or
(vi) a radical containing a 5- or 6-membered ring and a cyclopropane ring;

X represents
(i) a saturated or olefinically unsaturated aliphatic chain, which can be interrupted by hetero atoms such as oxygen, sulphur or the group NR^{II}, phenylene rings or cycloaliphatic rings,
(ii) a saturated or unsaturated cycloaliphatic radical, or
(iii) a single chemical bond;

Z represents



or nitrile

R^{II} represents hydrogen or a saturated olefinically unsaturated aliphatic group, or cycloalkyl,

R^{III} represents an aliphatic saturated or olefinically unsaturated group, or cycloalkyl, or

R^{II} and R^{III}, together with the nitrogen atom to which they are attached, represent the ring members required to complete a saturated heterocyclic ring.

2. A photosensitive material as claimed in claim 1, wherein Z represents the group

R^{II} and R^{III} as defined in claim 1.

3. A phososensitive material as claimed in claim 2, wherein X represents an aliphatic chain with 2 or 3 carbon atoms and R^{II} and R^{III} each represent methyl.

4. A photosensitive material as claimed in claim 2, wherein X represents a bivalent cyclohexane group.

5. A photosensitive material as claimed in claim 2, wherein R^{II} and R^{III} represent the ring members required to complete a pyrrolidine or pyrrolidone ring.

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U.S. Cl. X.R.

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