

[54] **PHOTO-THERMOGRAPHIC RECORDING  
PROCESS WITH 5-PYRAZOLANE**

[75] Inventors: **Albert Lucien Poot, Kontich; Jan  
Frans Van Besauw, Brasschaat, both  
of Belgium**

[73] Assignee: **Agfa-Gevaert N.V., Mortsel,  
Belgium**

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[58] **Field of Search** ..... **96/28, 90**

[56] **References Cited**

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*Primary Examiner*—Norman G. Torchin

*Assistant Examiner*—John L. Goodrow

*Attorney*—William J. Daniel

[57]

**ABSTRACT**

A photosensitive recording material containing a pyrazolin-5-one reducing agent having at least one hydrogen atom in its 4-position in chemical interreactive relationship with a photoreducible dye capable when exposed to activating electromagnetic radiation adsorbable by the dye of initiating oxidation of the pyrazolin-5-one reducing agent, whereby imagewise exposure of the material to such radiation causes the reducing properties of said pyrazolin-5-one agent to be substantially eliminated in the exposed areas thereof and an image recording method using the same. The material can also contain a bi-imidazolyl compound.

**9 Claims, No Drawings**

# PHOTO-THERMOGRAPHIC RECORDING PROCESS WITH 5-PYRAZOLANE

The present invention relates to photothermographic reproduction of information and to materials used therefor.

In a well known thermographic process a heat-sensitive copy sheet is used, which when heated beyond a certain temperature, turns black or dark coloured. In the process wherein such a copy sheet is used, the original containing infrared light-absorbing image areas is exposed to infrared radiation while being in heat-conductive contact with the copy sheet. In correspondence with the image areas of the original the copy sheet reaches a temperature at which a coloured product is formed. So, in this process heat is used, which is accumulated image-wise in the original and transferred therefrom to the copy sheet.

As there is no neutralizing action on the reactive components still present in the non-heated portions of the recording layer, the copy paper will remain heat-sensitive and the image-containing copy paper will be blackened completely by overall heating. This characteristic and the fact that this process is limited to the copying of originals containing infrared radiation-absorbing image-markings on an infrared radiation-reflecting background make that process less attractive.

In order to find a solution for the disadvantages of said process a photothermographic process has been developed as described in the U.S. Pat. No. 3,094,417 of Wesley R. Workmans, issued June 18, 1968.

In the latter process the difficulty of color-insensitivity and of image stabilization of the copy sheet is solved. In said process light and heat energy are used to produce the visible image and therefor it is called a dual spectrum process.

According to an embodiment of said process an intermediate photosensitive sheet is used for the information-wise exposure. The intermediate sheet includes a first reactant that becomes transformed with the aid of exposed photoreducible dye into a form that is unreactive for a second reactant contained in a receptor sheet. The photoreducible dye has been characterized by its ability to cause reduction of silver ions in a dilute solution of silver nitrate and triethanolammonium nitrate.

A photographic recording and reproduction process based on a photochemical reduction of photoreducible dyes has hitherto been mentioned, e.g., in the U.K. Pat. 903,942 filed July 26, 1960 by Gisela K. Oster and Gerard Oster (corresponding with U.S. Pat. 3,145,104 of Gisela K. Oster and Gerard Oster, issued Aug. 18, 1964). The chemicals being in inter-reactive relationship with the photo-reducible dye are polymers containing sulfhydryl groups. Said groups become oxidized on irradiation of the photoreducible dye and form disulphide groups crosslinking the polymer chains.

According to the process described in the aforesaid U.S. Pat. 3,094,417 the first and second reactant are capable of rapidly chemically inter-reacting at a conversion temperature between about 90° C and about 150° C with production of a visibly distinct reaction product.

The first and second reactants are characterized by a positive result in a test which conveniently is run as follows.

Given a visibly heat-sensitive system consisting essentially of two inter-reactant materials A and B, material A being said first reactant is first dissolved in an inert liquid solvent at low concentration. The solvent is selected to be non-reactive with either of the reactant materials, and neither absorbs nor is altered by the actinic radiation employed.

The concentration of material A is just sufficient to produce a distinctly visible reaction with material B being the second reactant. A portion of the solution is in a small transparent quartz test tube, is exposed to radiation of 3,000–4,200 Å. from a B-H6 high pressure mercury arc lamp at 6 inches from the sample for a time up to 45 minutes. A second portion is retained as a control. A small amount of material B is then mixed into each of the irradiated and the non-irradiated portions, with heating on a waterbath to about 60° C, where required, and the two solutions are compared for colour. A system in which the colour of the test solution is widely different or decidedly reduced in intensity from that of the control, is by definition according to the above-mentioned U.S. Pat. 3,094,417 a readily desensitizable system as that term is employed in that document and useful in the practicing the invention described therein. The B-A6 lamp is marketed by General Electric, U.S.A.; the output of the lamp in the wavelength region of 3,200–4,000 Å. is 109.3 Watt (see U.K. Pat. 966,694 filed Aug. 10, 1960 of Minesota Mining and Manufacturing Co.

First reactants or reactants A mentioned in connection with properly selected second reactants are: 4-methoxy-1-naphthol, dithiooxamide ascorbyl palmitate, 1-phenyl-dithiohydrazocarbonamide, N,N'-bis(p-toluenesulphonyl)-N,N'-dichloroethylenediamine, tin(II)sulphate, 2-methyl-5-hexadecyl-benzoquinone, N-nitroso-diphenylamine and 3,3'-dimethoxy-4,4'-diphenylene-bis(3-methyl-3-(sodium methylene carboxylate)-1-triazene.

One aspect of the invention makes use of the discovery that pyrazolin-5-one compounds containing at least one hydrogen atom in the 4-position are capable of reducing a noble metal salt of an organic acid at elevated temperature.

A further aspect of the invention is based on the fact that such pyrazoline-5-one compounds are capable of reaction with exposed photosensitive substances which during exposure are converted to a form which exerts an oxidizing function. A particular class of such photosensitive substances are the so-called photo-reducible dyes.

Although having the above properties most of the pyrazoline-5-one compounds used according to the present invention surprisingly do not give a result as desired in the above described test using a first reactant A and a second reactant B, and thus would not be capable of selection using such a test.

The following comparative tests illustrate the difference in behaviour of two particular pyrazolin-5-one compounds compared with 4-methoxy-1-naphthol described in U.S. Pat. No. 3,094,417 mentioned above.

Procedure  
Three 0.05 % by weight solutions in 2-butanone of the following substance (I), (II) and (III) were made:  
I. 4-methoxy-1-naphthol  
II. N-phenyl-3-methyl-pyrazolin-5-one  
III. N-(2,5-dichlorophenyl)-3-methyl-pyrazolin-5-one.

From each solution 10 ml were kept apart in the dark and 10 ml put in a small transparent quartz test tube. The three samples in the quartz test tube were exposed for 3 hours under the same conditions to ultra-violet radiation emitted by a high pressure mercury arc lamp HPR-125 Watt placed at a distance of 20 cm. (The HPR-lamp-125 Watt is marketed by N.V. Philips Gloeilampenfabrieken Eindhoven — Netherlands).

To each of the exposed samples and to the same quantity of unexposed samples 50 mg of silver behenate was added and every sample gradually heated on a water-bath till 95° C.

The exposed sample containing 4-methoxy-1-naphthol showed already before reaching the temperature of 60° C a substantial lower colour intensity when compared with the unexposed sample.

The heating of the exposed samples and unexposed samples containing the pyrazolin-5-ones showed even at 95° C neither a difference in colour nor a difference in intensity of colour detectable by the naked eye.

The colour produced at the temperatures of 60°–80° and 95° C respectively changed from grey over pale-brown to deep brown.

The following description is provided of an alternative comparative test to demonstrate the difference in behaviour of 4-methoxy-1-naphthol (product I) and N-(2,5-dichlorophenyl)-3-methyl-pyrazolin-5-one (product II) after exposure to ultraviolet light of a wavelength above 300 nm.

The exposure unit used in the test was a so-called photochemical reactor "RAYONET TYPE RS" provided with 4 "RUL 3500 A." tube like lamps having a total capacity of 800 W and emitting in the wavelength range of 300 to 400 nm.

The test was carried out with 0.005 % by weight solutions of products I and II in n-propanol.

From each solution 100 ml were placed in a pyrex glass tube having an inner diameter of 4 cm. The tubes were arranged parallel to the lamps at 10 cm. The exposure time was 45 min. A sample of each test solution was kept apart in non-exposed state.

The visible results of the colour reaction obtained by adding 25 mg of a mixture of silver behenate : behenic acid (1:1 by weight) to 10 ml of each sample are listed in the following table.

TABLE

Product	Unexposed sample	Exposed sample
I.....	Blue solution plus grey precipitate.	Yellow solution plus white precipitate.
II.....	Colourless solution plus ochreous precipitate.	Colourless solution plus ochreous precipitate.

So, product II (the pyrazolin-5-one) remained unchanged.

The absorption maximum of the pyrazolin-5-ones is below 320 nm viz. at about 280 nm and it is supposed that this is the reason why they do not show the test results encountered under the test conditions (320 to 400 nm) mentioned in the aforesaid U.K. Pat. No. 966,694.

According to the present invention the pyrazolin-5-one compounds are used preferably in a recording process containing the steps of :

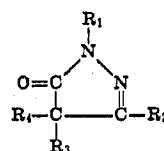
1. image-wise exposing to activating electromagnetic radiation a recording element containing a photo-

reducible dye being in inter-reactive chemical relationship with a said pyrazolin-5-one compound as a first reactant, the exposure being carried out for a time and with an intensity sufficient to cause a corresponding destruction of reducing capacity of pyrazolin-5-one molecules contained in the exposed portions, and

2. overall heating the recording element under conditions to allow the pyrazolin-5-one compound in the unexposed areas to come into contact, e.g., in situ or by physical transference with a second reactant with which by chemical reaction it forms a physically- or chemically-detectable change, for example a colour change.

According to a preferred embodiment of the invention a photothermographic recording process comprises using an intermediate recording material containing a transferable pyrazolin-5-one compound being in chemical interreactive relationship with a photoreducible dye which in a first step is information-wise exposed with electromagnetic radiation to activate the dye for the destruction of the reducing power of the pyrazolin-5-one compound in the exposed areas and wherein in a second step heat is applied to transfer unmodified reducing pyrazolin-5-one compound, e.g., by vapourisation or as a result of melting of a binding agent therefor (when present) from the intermediate sheet to a receiving material such as a receptor sheet containing a reducible substance with which the pyrazolin-5-one compound is capable of reacting to form a substance differing in colour from the reactants.

Pyrazolin-5-one compounds that are suitable for application in a recording process according to the present invention correspond to the following general formula :



wherein :

R<sub>1</sub> stands for hydrogen, an organic group, e.g., an aliphatic or carbocyclic group including said groups in substituted form, e.g., an alkyl group, preferably a C<sub>1</sub>-C<sub>8</sub> alkyl group, a cycloalkyl group, e.g. a cyclohexyl or cyclopentyl group, a substituted alkyl group, e.g., a benzyl group, a cyano alkyl group, a halogen substituted alkyl group, an amino-substituted alkyl group, a dialkyl aminoalkyl group, an aryl group, e.g., a phenyl group including a substituted aryl group, e.g., an aryl group substituted with substituents of the group of alkyl, halogen, amino, substituted amino, e.g., alkylated amino, alkoxy, nitro, acyl, and/or acylamino, a heterocyclic group including a substituted heterocyclic group, e.g., a benzothiazolyl group,

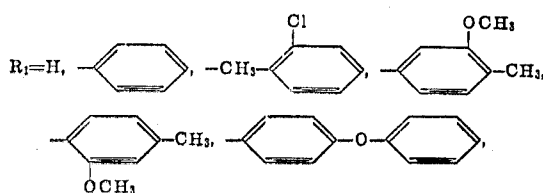
R<sub>2</sub> stands for hydrogen, an organic group, e.g., an aliphatic or carbocyclic group including said groups in substituted form, e.g., an alkyl group, preferably a C<sub>1</sub>-C<sub>8</sub> alkyl group, a cycloalkyl group, e.g., cyclohexyl or cyclopentyl, a substituted alkyl group, e.g., a benzyl group, a carboxy-substituted alkyl group, a halogen-substituted alkyl group, a hydroxyl-

substituted alkyl group, an alkoxy-substituted alkyl group, a hydroxyl group including an etherified hydroxyl group, an ester group, an amino group, a substituted amino group, e.g., an acylamino group, a substituted acylamino group, an ureido group, a substituted ureido group, a thioureido group, a N-carbamic ester group, a carbonamide group (-CONH<sub>2</sub>), an aryl group, e.g., a phenyl group, a substituted aryl group, e.g., substituted with alkyl, alkoxy, nitro or halogen, e.g., chlorine, bromine or 10 fluorine, a heterocyclic group, including a substituted heterocyclic group, e.g., a pyridyl group,

R<sub>3</sub> stands for hydrogen, a saturated or olefinic unsaturated aliphatic group e.g. a C<sub>1</sub>-C<sub>6</sub> alkyl group including such groups in substituted form, e.g., substituted with phenyl as in benzyl and phenylethyl, with halogen, e.g., chlorine or bromine, with a cyano group, with an alkoxy group, with an alkoxy carbonyl group or with an anilino carbonyl group, a dialkyl amino alkyl group, an aryl group including a substituted aryl group, e.g., a phenyl group or an aryl group substituted with alkyl or alkoxy preferably containing 3 carbon atoms, with a nitro group or with a nitrile group, an amino group including a substituted amino group, e.g., a C<sub>1</sub>-C<sub>3</sub> alkylated amino group, a cycloalkyl substituted amino group, a phenyl substituted amino group, an acyl substituted amino group preferably containing an acyl group of short chain aliphatic carboxylic acids, an alkoxy group preferably a C<sub>1</sub>-C<sub>3</sub> alkoxy group, halogen, e.g., chlorine or a -CONH<sub>2</sub> group,

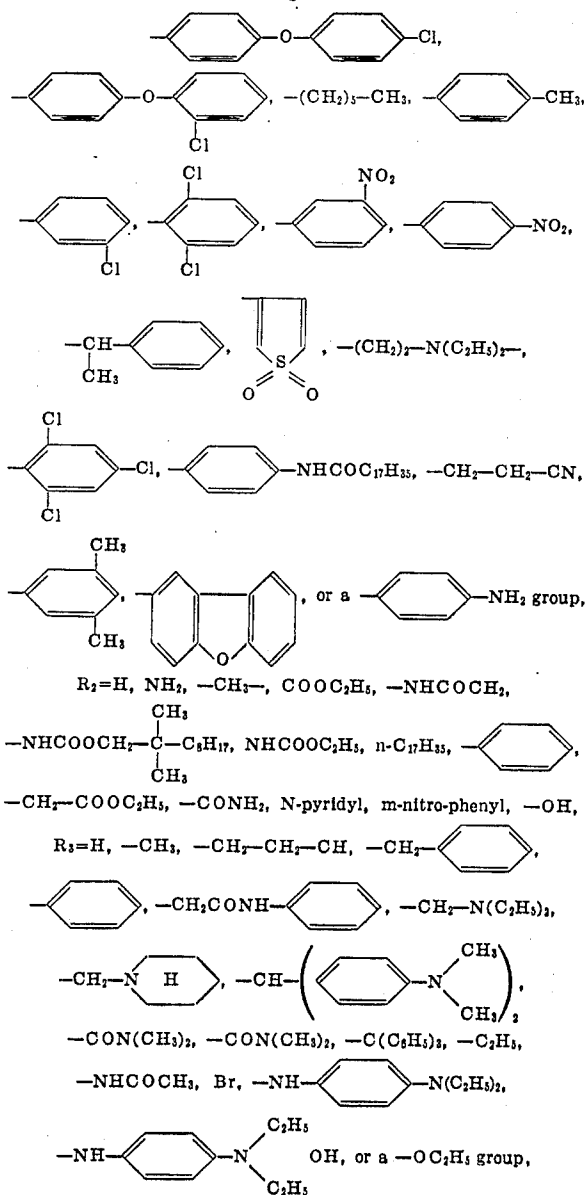
R<sub>4</sub> stands for hydrogen, or an alkyl group, e.g., a C<sub>1</sub>-C<sub>5</sub> alkyl group, or a 4-amino phenylamino group, at least one of the substituents R<sub>3</sub> or R<sub>4</sub> 35 being hydrogen.

The following is a list of suitable R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> substituents of pyrazolin-5-one compounds applicable in the present invention :



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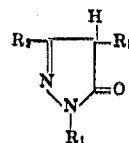


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R<sub>4</sub> = H or a -CH<sub>3</sub> group.

Preferred pyrazolin-5-one compounds are listed in the following Table.

TABLE



Pyrazolin-5-one number	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
1.....	C <sub>2</sub> H <sub>5</sub> .....	NH <sub>2</sub> .....	H.....
2.....	H.....	CH <sub>3</sub> .....	H.....
3.....	C <sub>2</sub> H <sub>5</sub> .....	CH <sub>3</sub> .....	H.....
4.....	Cyclohexyl.....	CH <sub>3</sub> .....	H.....
5.....	p-Tolyl.....	CH <sub>3</sub> .....	H.....
6.....	m-Chlorophenyl.....	CH <sub>3</sub> .....	H.....
7.....	2,6-dichlorophenyl.....	CH <sub>3</sub> .....	H.....
8.....	3-nitrophenyl.....	CH <sub>3</sub> .....	H.....
9.....	4-nitrophenyl.....	CH <sub>3</sub> .....	H.....
10.....	C <sub>2</sub> H <sub>5</sub> .....	-COOC <sub>2</sub> H <sub>5</sub> .....	H.....

Table - Continued

Pyrazolin-5-one number	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
11.....	1-phenylethyl.....	C <sub>6</sub> H <sub>5</sub> .....	H.....
12.....	C <sub>6</sub> H <sub>5</sub> .....	-CH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub> .....	H.....
13.....	C <sub>6</sub> H <sub>5</sub> .....	Pyridyl-4.....	H.....
14.....	2-diethylaminoethyl.....	CH <sub>3</sub> .....	H.....
15.....	2,4,6-trichlorophenyl.....	CH <sub>3</sub> .....	H.....
16.....	2,4,5-trichlorophenyl.....	CH <sub>3</sub> .....	H.....
17.....	2-cyanethyl.....	C <sub>6</sub> H <sub>5</sub> .....	H.....
18.....	3,5-dimethylphenyl.....	-COOC <sub>2</sub> H <sub>5</sub> .....	H.....
19.....	C <sub>6</sub> H <sub>5</sub> .....	OH.....	H.....
20.....	3-nitrophenyl.....	CH <sub>3</sub> .....	CH <sub>3</sub> .....
21.....	3-aminophenyl.....	CH <sub>3</sub> .....	CH <sub>3</sub> .....
22.....	3-nitrophenyl.....	CH <sub>3</sub> .....	Benzyl.....
23.....	2-ethoxyphenyl.....	C <sub>6</sub> H <sub>5</sub> .....	CH <sub>3</sub> .....
24.....	C <sub>6</sub> H <sub>5</sub> .....	C <sub>6</sub> H <sub>5</sub> .....	CH <sub>3</sub> .....
25.....	C <sub>6</sub> H <sub>5</sub> .....	C <sub>6</sub> H <sub>5</sub> .....	C <sub>6</sub> H <sub>5</sub> .....
26.....	C <sub>6</sub> H <sub>5</sub> .....	-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -	
27.....	C <sub>6</sub> H <sub>5</sub> .....	CH <sub>3</sub> .....	-CH <sub>2</sub> CO-NHC <sub>6</sub> H <sub>5</sub> .....
28.....	C <sub>6</sub> H <sub>5</sub> .....	-COOC <sub>2</sub> H <sub>5</sub> .....	CH <sub>3</sub> .....
29.....	C <sub>6</sub> H <sub>5</sub> .....	-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -S-	
30.....	3-nitrophenyl.....	CH <sub>3</sub> .....	C <sub>6</sub> H <sub>5</sub> .....
31.....	C <sub>6</sub> H <sub>5</sub> .....	CH <sub>3</sub> .....	-NHCOCH <sub>3</sub> .....
32.....	C <sub>6</sub> H <sub>5</sub> .....	-COOC <sub>2</sub> H <sub>5</sub> .....	-OC <sub>2</sub> H <sub>5</sub> .....
33.....	C <sub>6</sub> H <sub>5</sub> .....	CH <sub>3</sub> .....	CH <sub>3</sub> .....
34.....	1-[benzothiazolyl-2]-3,4-dimethyl-4-[4-diethylaminophenylamino]-pyrazolin-5-one.....		
35.....	1-phenyl-3,4-dimethyl-4-[4-diethylaminophenylamino]-pyrazolin-5-one.....		

The pyrazolin-5-one compounds containing at least one hydrogen atom in 4-position are well known intermediate products in the preparation of magenta azomethine dyes and are widely used for the manufacture of photographic silver halide colour materials.

The pyrazolin-5-one compounds can be prepared by condensation of a proper hydrazine with a selected active methylene keto compound such as an acyl acetic ester. For the preparation of particular pyrazolin-5-one compounds reference is made to the literature concerning the preparation of pyrazolones useful in colour photography, e.g., to Glafkides' Photographic Chemistry, Vol. II, Fountain Press, London (1960), 601, and the U.S. Pat. Nos. 3,462,270 of Hector Alfons Vanden Eynde, Robert Joseph Pollet, Arthur Henri De Cat, issued Aug. 19, 1969, 3,325,482 of Marcel Jacob Monbaliu, Arthur Henri De cat and Raphael Karel Van Poucke, issued June 13, 1967, and 3,393,071 of Marcel Jacob Monbaliu, Arthur Henri De Cat and Raphael Karel Van Poucke.

Operable photosensitive dyes can be distinguished by means of a simple chemical test performed in solution and involving the reduction of silver ion to metal. The procedure of that test has been described in the above-mentioned U.S. Pat. No. 3,094,417 and operates as follows:

A solution is prepared in an inert neutral light-stable liquid solvent containing per litre of solution approximately 0.001 mole of silver nitrate, 0.01 mole of triethanolammonium nitrate (prepared, for example, by neutralizing triethanolamine with nitric acid), and 0.0001 mole of the dye. The concentrations are not critical but should be of the indicated order of magnitude. Water is a preferred solvent where the dye to be tested is soluble therein; methanol, dioxane, or mixtures of these with water are useful with dyes that are insoluble or partially soluble in water alone. Two 15 ml portions are placed in Pyrex test tubes in a water-bath at 50° C. One is protected from light whereas the other is irradiated for 30 minutes with light from a 500 Watt tungsten filament projection bulb at a distance of 8 inches from the sample, i.e., at an intensity of about 60,000 foot-candles. The two tubes are then visually compared. The control tube is found to contain a visible trace of precipitated silver, ordinarily as a fine

black powder. In the presence of an activatable dye, the amount of silver precipitated from the test solution is significantly increased. Large increases may be estimated visually, or the amounts of precipitate may be determined by quantitative analysis. Precipitation of silver under test conditions may occur in the form either of dense black flakes or of a silver mirror on the clean wall of the tube. Although not ordinarily required, the silver precipitate may be distinguished from precipitated portions of dye or other materials by its insolubility in excess of organic solvent.

Copious precipitation of silver occurs in the just-described test when applied to halogen-containing fluorescein dyes, e.g., erythrosin, Rose Bengale, D & C Orange 16, and Aizen Acid Phloxine PB, and to pararosaniline dyes, e.g., Calcozine Violet Ex.Conc.

Additional examples of dyes that have been found to be less effective but still useful for the purposes of the invention include Eosin OJ Purified, Rhodamine B Extra S, Pontacyl Violet S4B, Pontachrome Azure Blue B, Phenosafranin, Fast Fat Blue B, Artisil Orange 3RP, Tinon Yellow GK-F, Calcozine Blue ZF (methylene blue), Aizen New Methylene Blue NHX, Seto Flavine T, proflavine hydrochloride, Azo Scarlet Y, and Kryptocyanine. Mixtures of dyes may be used. In each instance the dye is a coloured organic compound that absorbs light in the visible wavelength range above about 420 nm, which causes reduction of silver ion and precipitation of metallic silver under the test conditions hereinbefore described, and which reduces under irradiation with visible light the reducing power the pyrazolin-5-ones have at elevated temperatures, e.g., at 90-150° C.

Another test that can be used to determine whether an operable dye is at the disposal or not makes use of the photo-oxidation by means of these dyes of a compound containing a sulfhydryl group, e.g., a thiol polymer.

Dyes that on irradiation with visible light sensitize the oxidation of the sulfhydryl groups of a thiol polymer are described, e.g., in the U.K. Pat. 903,942 mentioned above. These dyes include rose bengal, phloxine, erythrosine, eosin, fluorescein, acriflavine, thionine, riboflavin, chlorophylls, hematoporphyrin, proflavine, methylene blue, and the like. The dyes thus include members of the fluorescein family, the thiazine family, and

certain acridines and porphyrins. A large number of these dyes are characterized by their fluorescence and are described, e.g., in U.S. Pat. 2,850,455 of Rudolf Kern and Hans Scheurer, issued Sept. 2, 1958 and 2,857,047 of Dorothy R. Edelson, issued Oct. 21, 1958.

Although the amount of photoreducible dye may be varied over wide ranges in respect of the pyrazolin-5-one compound, it is preferred to employ minimal amounts so that the light may readily penetrate the dyed coating and allow a reflux exposure in combination with opaque originals having differentially light-absorptive image and background areas.

The light-sensitive sheets used according to the present invention contain at least one pyrazolin-5-one compound in a ratio of preferably 1 mole to 0.1-0.2 mole of photo-reducible dye(s). Preferably, the pyrazolin-5-one compound is applied in an amount of 0.1 to 1.5 g per sq.m., but the amount can be adapted according to the requirements of the copying process and the kind of photoreducible dye(s) and reducible substance in the receptor layer or sheet.

For the preparation of the photosensitive material the photoreducible dye(s) and the reducing pyrazolin-5-one compound, which is transferable by heat in volatilized or molten state, are applied together from a solution or dispersion preferably in the presence of a film-forming binding agent to a suitable support.

As binding agent for the photosensitive layer all kinds of natural, modified natural and synthetic resins can be used, e.g., proteins such as gelatin, cellulose derivatives, e.g., a cellulose ether such as ethylcellulose, cellulose esters, carboxymethyl cellulose, alginic acid and derivatives, starch ethers, galactomannan, polyvinyl alcohol, poly-N-vinylpyrrolidone, polymers derived from  $\alpha,\beta$ -ethylenically unsaturated compounds, e.g., homo- and co-vinyl polymers such as polyvinyl chloride, copolymers of vinyl chloride and vinyl acetate partially saponified polyvinyl acetate, copolymers of acrylonitrile and acrylamide, polyacrylic acid esters, polymethacrylic acid esters, or polyethylene.

The ratio by weight of pyrazolin-5-one compound to binder is e.g., 0.02-0.3.

The photosensitive material may consist of a self-supporting sheet or may comprise a photosensitive layer applied to a support. Suitable supports are, e.g., supports of paper of which glassine paper is preferred, and resin supports known in silver halide photography. It is also possible to apply the photosensitive material to glass or to a support from which it can be stripped off and transferred to a permanent support.

A receptor layer or separate material used in conjunction with a photosensitive material applied an intermediate sheet contains a substance that is a reactive component in a colour reaction with the reducing pyrazolin-5-one contained in the photosensitive sheet.

Such substances belong to a wide diversified group of chemicals so that it is practically impossible to characterize them by a particular chemical structure.

A practical test that can be used to know whether a particular reducible compound used in a receiving layer or sheet is suited or not to produce a visible colour change with the pyrazolin-5-one compound is to heat the elected reaction partners in one of the above binding agents or an inert solvent beyond a temperature of 60° C with a particular reaction partner to be used in the receiving layer or sheet, and to take notice,

e.g., between 80° and 120° C of the degree of colour change in the layer or test tube.

The pyrazolin-5-compounds have a particularly high reactivity with the photo-exposed photo-reducible dyes, which is important in order to obtain clear copies in the receptor layer or sheet within a suitable exposure and processing time.

Reaction partners for the reducing pyrazolin-5 one compounds are, e.g., :

I. Noble metal compounds e.g. silver compounds, which under the conditions of the copying process of the present invention are extremely non-light sensitive, e.g., the silver salts of aliphatic carboxylic acids with a thioether group such as described, e.g., in the U.K. Pat. 1,111,492 filed Aug. 13, 1965 by Agfa AG, or silver salts of long chained aliphatic (at least C<sub>14</sub>) carboxylic acids such as silver behenate, silver palmitate, silver stearate and others.

II. Diazonium salts that are reactive with the pyrazolin-5-one compound through the active hydrogen atom(s) present in 4-position to the 5-one group. By coupling known from diazotype chemistry the diazonium salts form a dye with said pyrazolones.

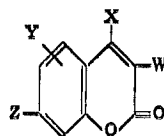
III. Compounds that in oxidized form or under oxidizing conditions produce a coloured substance with the pyrazolin-5-one, e.g., p-phenylenediamine and derivatives thereof that form azo-methine dyes known from silver halide colour photography.

In addition to the actual image-forming reaction partners the layer or sheet in which the image is formed may contain further additives, e.g., toning agents e.g. 1-(2H)-phthalazinone, and agents which accelerate the reaction for the formation of the image substance, e.g., sterically hindered phenols that on heating become reactive partners in the reduction reaction, e.g., 2,4,6-tri-tert. butylphenol. Suitable image-receiving layers are known already, e.g., from the U.S. Pat. Nos. 3,094,417 precited, 3,094,619 of Edwin A. Grant Jr., issued June 18, 1963 and 3,094,620 of John L. Reitter, issued June 18, 1963, the German Pat. Nos. 895,101 filed Nov. 10, 1944 by I.G. Forbenindustrie, 1,003,577 filed Feb. 11, 1955 by Agfa AG, 1,159,758 filed Sept. 24, 1962 by Agfa AG, 1,004,043 filed Feb. 7, 1955 by Agfa AG and 1,165,410 filed Sept. 15, 1962 by Agfa AG, the published Dutch Pat. application No. 277,086 filed Apr. 11, 1962 by Gevaert Photo-Producten N.V. and the Belgian Pat. Nos. 614,064 filed Aug. 20, 1962 and 609,057 filed Apr. 12, 1962, both by Gevaert Photo-Producten N.V.

The spectral sensitivity of the photo-sensitive materials depends on the type of the photo-reducible dye used and the enlargement and/or enhancement of the spectral sensitivity by means of spectral sensitizing dyes.

The photoreducible dyes may be used in admixture with photooxidantia such as the bi-imidazolyl compounds described in the U.K. Pat. No. 997,396 filed Mar. 21, 1963 by du Pont de Nemours.

These photo-oxidantia can be spectrally sensitized. For example the bi-imidazolyl compounds can be spectrally sensitized by means of fluorescing coumarin derivatives having the following general formula :



wherein :

each of X and Y represents hydrogen, an alkyl group, including a substituted alkyl group, or an alkoxy group,

Z represents hydrogen, an alkyl group including a substituted alkyl group, an alkoxy group, an amino group, including a substituted amino group preferably a dialkylamino group, and

W represents hydrogen, an alkyl group including a substituted alkyl group, an aryl group, including a substituted aryl group, e.g. a phenyl group having in the o- or p-position an alkoxy or dialkylamino group.

Preferably the coumarin derivative contains a dialkylamino group or alkoxy group in 3 and/or 7 position of the coumarin nucleus.

The biimidazolyl compounds are inherently sensitive to ultraviolet light of a wavelength below 300 nm.

The biimidazolyl compounds can further be spectrally sensitized advantageously by means of sensitizing dyes known as spectral sensitizing agents in silver halide photography.

Preferably used are cyanine dyes, merocyanines, styryl dyes and rhodacyanines of all sorts, e.g., as described by F.M. Hamer in his book : "The Cyanine Dyes and Related Compounds," 1964, e.g., as described on pages 90, 100, 433, 502 and 511.

The most suitable sensitizing agents for a photo-reducible dye, or a particular biimidazolyl compound can be determined by means of the usual sensitometric tests, without difficulty by those skilled in the art.

By the addition of sensitizing agents not only an increase of sensitivity is reached but also a marked increase of the general sensitivity, which is desirable for obtaining shorter times of copying. Thanks to the possibility of spectral sensitization of recording layers according to this invention also for the red and green regions of the spectrum it is possible not only to copy coloured originals in an unobjectional way but also to prepare copies in natural colours by a suitable choice of the image-forming systems, which yield dyestuffs in the subtractive selection colours.

The information-wise exposure may be carried out by means of visible light produced, e.g., with an incandescent or fluorescent lamp.

The exposure time and intensity are preferably the time and light-intensity required to destroy the ability of the recording material to produce a visible reaction when heated in contact with a silver behenate-containing receptor sheet.

Heat may be applied to the exposed recording material in any way. It has to allow and/or to promote the chemical reaction producing the visible image. For example heat may be supplied from heated plates or rollers, from an infrared radiation source, by means of an electric resistance or high-frequency current heating source.

The present invention makes it possible to produce by reflex-exposure a visible positive directly legible image on receiving sheets containing an image-forming reactant for the pyrazolin-5-one compound transferred from a photosensitive intermediate sheet. The copies need not to be stabilized and have a substantially colourless background.

Although for the production of visible images on a very clear image background preferably the combination of intermediate sheet and receptor sheet is used, it is possible to obtain according to the present inven-

tion copies in a unitary photothermosensitive copy sheet. For that purpose techniques can be applied as described in the U.S. Pat. No. 3,094,417 mentioned above.

So, e.g., a copy sheet may be used comprising on a thin transparent paper-like backing a thin coating containing a substance that can form a coloured product by reaction with the pyrazolin-5-one compound, but is kept out of direct chemical contact with said compound.

Direct chemical contact can be avoided, e.g., by means of a thin non-transparent highly pigmented vapour-permeable binder layer the binding agent of which is not soluble in the solvent from which the photosensitive top-coat is applied.

The unitary photo-thermosensitive copy sheet when applied in a reflex exposure technique yields a copy that is directly legible through the rear side of the transparent support.

A pigment such as titanium dioxide and zinc oxide having an average grain size of 5 to 1  $\mu$  allows the penetration on heating of a vaporizable pyrazolin-5-one compound through a binder such as ethylcellulose.

The permeable layer may alternatively be replaced by a normally impermeable thin coating of a fusible film-forming material, which melts and becomes compatible (see the U.K. Pat. No. 1,184,054 filed Apr. 5, 1966 by Gevaert-Agfa N.V. and the U.S. Pat. 3,223,838 of Shoichiro Hoshino and Akira Kato, issued Dec. 14, 1965) with the underlying binder medium for the reducible substance.

Instead of transferring the reducing agent in volatilized state it is possible to transfer it in a fusible medium, e.g., a fusible waxy or resinous medium. Transfer can be speeded up by using a solvent causing some swelling as described in the U.K. Pat. 1,135,371 filed Jan. 7, 1966 by Agfa AG. Heat transfer of polymer substrata without solvent swelling is described, e.g., in the Belgian Pat. No. 700,472 filed Dec. 27, 1967 by Gevaert Photo-Producten N.V. corresponding with the U.K. Pat. No. 1,195,842 filed June 24, 1966 by Gevaert-Agfa N.V.

The following examples illustrate the present invention without, however, limiting it thereto. The percentages are by weight when no otherwise indicated.

#### Example 1

To a map overlay tracing paper the following composition was applied in a ratio of 25 g/sq.m :

n-(2,5-dichlorophenyl)-3-methyl pyrazolin-5-one	1 g
erythrosin	440 mg
ethylcellulose	50 g
methyl ethylketone up till	500 g

After drying the photosensitive coating was exposed in reflex to a graphic original having differentially light-absorptive image and background areas. The copy sheet was hereby placed with its coated surface in contact with the printed text of the original. The exposure lasted 30 sec. and was effected by means of a tungsten filament light source of 1,500 watt placed at a distance of 5 cm from the copy sheet.

Subsequently the irradiated sheet was pressed for 5 sec. with its photosensitive layer in contact at 125° C with a receptor sheet, which is a white paper prepared

by coating and drying thereon a continuous thin colourless layer of a ball-milled mixture of silver behenate, phthalazinone as toning agent, 2,6-di-tert-butyl-4-methylphenol as heat-sensitive reductor, poly-tert-butyl methacrylate as binding agent (three parts for every 10 parts of silver behenate) and 86 parts of acetone. The dried receptor sheet contained per sq.m an amount of silver behenate equivalent with 0.2 g of silver per sq.m, 400 mg of phthalazinone per sq.m, and 40 mg of 2,6-di-tert-butyl-4-methylphenol per sq.m.

A direct legible sharp, positive, dark brown copy of the original was obtained.

#### Examples 2-3

Example 1 was repeated but instead of using the mentioned pyrazolin-5-one, N-(2-chlorophenyl)-3-methyl-pyrazolin-5-one and N-(4-nitrophenyl)-3-methyl-pyrazolin-5-one were used respectively.

#### Example 4

Example 1 was repeated, but the mentioned pyrazolin-5-one was replaced by N-(phenyl)-3,4-dimethyl-pyrazolin-5-one.

A grayish-brown copy was obtained.

We claim :

1. An image recording method which comprises image-wise exposing to activating electromagnetic radiation a photosensitive recording layer containing a pyrazolin-5-one reducing agent having at least one hydrogen atom in its 4-position and in chemically inter-reactive contact with said agent a photoreducible dye adapted to be activated by said radiation and when activated to initiate oxidation of said reducing agent in the exposed areas of said layer to substantially eliminate the reducing properties of said agent in such areas while such properties in the unexposed areas remain unimpaired.

2. The method of claim 1 wherein said pyrazolin-5-one reducing agent is volatile when heated and including the steps of bringing said radiation exposed recording layer into contact with an image-forming layer

containing a chemical compound reactive with said reducing agent in its unoxidized form to produce a colored reaction product and uniformly heating said recording layer while in contact with said image-forming layer to transfer volatilized reducing agent from the unexposed areas of the recording layer to the contacting areas of the image-forming material and produce a reaction product image therein.

3. A method according to claim 1, comprising the steps of :

1. image-wise exposing to activating electromagnetic radiation a photosensitive recording material containing in admixture in a layer of a binder medium a volatilizable pyrazolin-5-one agent and said dye, and

2. uniformly heating said exposed material while being in intimate contact with a receiving material containing a substance that at the applied temperature react with the transferred pyrazolin-5-one compound forming (a) coloured product(s).

4. A method according to claim 3, wherein the receiving material contains a substantially non-light insensitive noble metal salt.

5. A method according to claim 3, wherein the exposure is a reflex contact exposure to a graphic original having differentially light-absorptive image and background areas.

6. A method according to claim 4, wherein the noble metal salt is silver behenate.

7. The method of claim 1 wherein said pyrazolin-5-one is a reducing agent for silver ions.

8. The method of claim 2 wherein said reactive compound is a noble metal salt, a diazonium salt, or a p-phenylene-diamine compound.

9. The method of claim 1 wherein said photosensitive recording layer also contains a bi-imidazolyl compound in admixture with said photoreducible dye.

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