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PHOTOGRAPHIC DRY COPYING MATERIAL

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ABSTRACT OF THE DISCLOSURE

Photographic copies are produced by image-wise exposing a light-sensitive layer which contains a light-sensitive photo-oxidizing compound and an image-producing pyrazolin-5-one capable of being transferred to an image-receiving layer, the image-producing compound in the exposed areas being converted into a non-transferable compound by reaction with the light-sensitive compound, bringing the exposed layer into contact with an image-receiving layer which contains compounds which react with the image-producing compound to form colored compounds and heating of the layers while in contact with each other to a temperature of between 80 and 200° C. at which the image-producing compound is transferred from the unexposed areas of the light-sensitive layer to the image-receiving layer.

The invention relates to a photographic dry copying process and to a light-sensitive material for carrying out this process.

Dry photographic processes for producing copies of an original are already known. The materials used for these processes consist mainly of layers which are sensitive to light or heat and which are either exposed to light or are heated. A color-forming reaction is thus initiated which leads to the formation of the image.

The known light-sensitive materials of this kind which can be used for producing negative copies have, however, several disadvantages. Their sensitivity to light is unsatisfactory, especially in the visible region of the spectrum, so that the copying times required are too long and the reproduction of colored original copies gives rise to difficulties. Moreover, the finished copies remain sensitive to light and their stabilisation against daylight can generally only be achieved by a very complicated after-treatment.

Other copying processes are known in which a light-sensitive layer which contains a light-sensitive compound and an image-producing compound which can be transferred to an image-receiving layer is exposed to light to convert the image-producing compound in the exposed areas into a non-transferable compound, the exposed layer is brought into contact with an image-receiving layer which contains compounds which react with the image-producing compound to form colored compounds, and the layers in contact with each other are heated to a temperature at which the image-producing compound is transferred from the unexposed areas of the light-sensitive layer to the image-receiving layer.

These processes include e.g. the so-called heat development processes in which the light-sensitive materials used include a silver halide emulsion layer which contains a photographic developing agent. After exposure, the photographic material is developed by heating it in contact with an image-receiving layer which contains substances which react with the developing agent to yield colored compounds. The developing agent is transferred by the heat from the unexposed areas of the light-sensitive layer to the image-receiving layer so that a colored image is produced in the corresponding areas of the receiving layer.

One disadvantage of this known heat development or developer-sublimation process is that the silver halide emulsion layers which contain developing agents are not sufficiently stable on storage. This is because they contain substances which increase the residual moisture content of the layers, e.g. salts which form hydrates, or glycols, and because of the increased sensitivity to oxidation of most developing agents in these unhardened or only slightly hardened emulsion layers which have a high residual moisture content.

The process described in U.S. Pat. No. 3,094,417 belongs to this type of copying process. The light-sensitive layers used in this process contain a volatile compound and a dye. On exposure, the volatile compound (4-methoxy-1-naphthol) is converted into a non-volatile product. This compound can be transferred by subsequent heating from the unexposed areas into an image-receiving layer where it reacts with a silver salt (silver behenate) to produce a colored positive image.

The last mentioned process has the disadvantage that the compounds which produce the image are insufficiently stable to atmospheric oxygen so that the material can only be kept for a limited time.

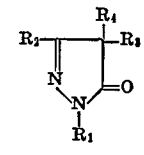
It is among the objects of the present invention to provide photographic dry copying processes and light-sensitive materials which are suitable for this process and which have sufficient sensitivity to light and storage stability and which enable colored and black-and-white images to be produced.

We now have found a dry copying process including the steps of imagewise exposing a supported light-sensitive layer containing as light-sensitive compound a photo-oxidizing agent and an image-producing compound capable of being transferred to an image-receiving layer whereby the image-producing compound in the exposed areas is converted into a non-transferable compound, contacting the exposed layer with an image-receiving layer which contains compounds which react with the image-producing compound to form colored compounds and heating of the layers while in contact with each other to a temperature at which the image-produced compound is transferred from the unexposed areas of the light-sensitive layer to the image-receiving layer; wherein the light-sensitive layer which contains a photooxidans contains, as image-producing, transferable compound, a pyrazolin-5-one which is transferable at a temperature of between 80° C. and 200° C.

A particular advantage of the pyrazolin-5-ones according to the present invention is their very low sensitivity to atmospheric oxygen.

The pyrazolin-5-ones preferably used are those pyrazolin-5-one derivatives which contain at least one hydrogen or a 4-aminophenylamino group in the 4-position.

Pyrazolin-5-one compounds of the following formula are particularly suitable:



In the above formula

R_1 is either

(1) hydrogen,

(2) a saturated or an olefinically unsaturated aliphatic group which preferably contains up to 6

carbon atoms and may be substituted, e.g. with phenyl as in the benzyl group with nitrile, halogen such as fluorine, with amino, in which case the amino group may in turn be substituted, e.g. alkylated amino groups and especially dialkylamino, the alkyl groups on the amino group preferably containing up to 3 carbon atoms,

(3) aryl, especially a group of the phenyl series; the aryl ring may in turn be substituted, e.g. with alkyl or alkoxy, preferably containing up to 3 carbon atoms, nitro, halogen such as fluorine, chlorine or bromine, amino or substituted amino group, e.g. alkylated amino groups,

(4) a heterocyclic group, e.g., benzothiazolyl, or

(5) a cycloalkyl group such as cyclohexyl or cyclopentyl;

R_2 represents

(1) hydrogen,

(2) a saturated or an olefinically unsaturated aliphatic group which preferably contains up to 6 carbon atoms and may itself be substituted e.g. with phenyl, as in the case of a benzyl or phenylethyl group with halogen such as fluorine, with alkoxy carbonyl, hydroxyl or alkoxy,

(3) aryl, especially a group of the phenyl series, the aryl ring may be substituted e.g. with alkyl or alkoxy, preferably containing up to 3 carbon atoms or with nitro or halogen such as chlorine or bromine,

(4) a heterocyclic group, e.g. pyridyl,

(5) cycloalkyl such as cyclohexyl or cyclopentyl,

(6) hydroxyl,

(7) alkoxy having preferably up to 3 carbon atoms,

(8) amino which may be substituted e.g. with alkyl preferably containing up to 3 carbon atoms, and

(9) an alkoxy carbonyl group having up to 5 carbon atoms;

R_3 stands for

(1) hydrogen,

(2) a saturated or an olefinically unsaturated aliphatic group which preferably contains up to 6 carbon atoms and which may be substituted e.g. with phenyl as in the case of benzyl or phenylethyl groups, with halogen such as chlorine or bromine, with nitrile, alkoxy having preferably up to 3 carbon atoms, alkoxy carbonyl or anilinocarbonyl,

(3) aryl, especially a group of the phenyl series, the aryl ring may be in turn substituted e.g. with alkyl or alkoxy preferably containing up to 3 carbon atoms, nitro or nitrile,

(4) amino which may be substituted e.g. with alkyl preferably containinng up to 3 carbon atoms, cycloalkyl, phenyl or acyl, especially acyl groups of short-chained aliphatic carboxylic acids, or

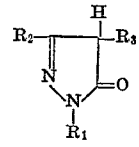
(5) alkoxy preferably containing up to 3 carbon atoms;

R_4 represents hydrogen, a 4-aminophenylamino group, a 4-alkylaminophenylamino group or a 4-dialkylaminophenylamino group.

Furthermore, R_2 and R_3 may together represent the ring members required to complete a 5-membered or 6-membered carbocyclic or heterocyclic ring.

Suitable compounds are shown in the following table:

TABLE I



Pyrazolin-5-one number	R_1	R_2	R_3
1	C_6H_5	NH_2	H
2	H	CH_3	H
3	C_6H_5	CH_3	H
4	Cyclohexyl	CH_3	H
5	P-tolyl	CH_3	H
6	m-Chlorophenyl	CH_3	H
7	2, 5-dichlorophenyl	CH_3	H
8	3-nitrophenyl	CH_3	H
9	4-nitrophenyl	CH_3	H
10	C_6H_5	$-COOC_2H_5$	H
11	1-phenylethyl	C_6H_5	H
12	C_6H_5	$-CH_2COOC_2H_5$	H
13	C_6H_5	Pyridyl-4	H
14	2-diethylaminoethyl	CH_3	H
15	2, 4, 6-trichlorophenyl	CH_3	H
16	2, 4, 5-trichlorophenyl	CH_3	H
17	2-cyanoethyl	C_6H_5	H
18	3, 5-dimethylphenyl	$-COOC_2H_5$	H
19	C_6H_5	OH	H
20	3-nitrophenyl	CH_3	CH_3
21	3-aminophenyl	CH_3	CH_3
22	3-nitrophenyl	CH_3	Benzyl
23	2-ethoxyphenyl	C_6H_5	CH_3
24	C_6H_5	C_6H_5	CH_3
25	C_6H_5	C_6H_5	C_2H_5
26	C_6H_5	$-CH_2-CH_2-CH_2-CH_2-$	
27	C_6H_5	CH_3	$-CH_2CO-NHC_6H_5$
28	C_6H_5	$-COOC_2H_5$	CH_3
29	C_6H_5	$-CH_2-CH_2-CH_2-S-$	
30	3-nitrophenyl	CH_3	C_2H_5
31	C_6H_5	CH_3	$-NHCOCH_3$
32	C_6H_5	$-COOC_2H_5$	$-OC_2H_5$
33	C_6H_5	CH_3	CH_3
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		
36	4-methyl-2-thiazolyl	CH_3	H
37	4-pyridyl	CH_3	H
38	2-pyridyl	CH_3	H
39	2-chloro-5-pyridyl	CH_3	H
40	2-quinolyl	CH_3	H
41	C_6H_5	2-thienyl	H
42	C_6H_5	2-furyl	H
43	C_6H_5	3, 5-dimethyl-2-pyrryl	H
44	p-Bromophenyl	2-furyl	H

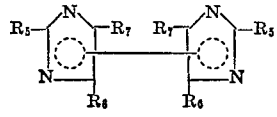
TABLE I—Continued

Pyrazolin-5-one number	R_1	R_2	R_3
45	C_6H_5	3-pyridyl	H
46	H	C_3H_7	H
47	C_2H_5	CH_3	H
48	C_4H_9	CH_3	H
49	C_6H_5	C_2H_5	H
50	C_6H_5	CF_3	H
51	C_6H_5	C_3H_7	H
52	C_6H_5	Cyclopropyl	H
53	C_6H_5	Cyclohex-1-enyl	H
54	3-nitrophenyl	Phenyl	Phenyl
55	3-nitrophenyl	C_2H_5O	H

The pyrazolin-5-one derivatives are prepared by methods known from the literature. See, for example, the monograph by Wiley "Pyrazolones, Pyrazolidones and Derivatives" (1964), Interscience Publishers, New York and German patent specification No. 1,155,675.

The light-sensitive photo-oxidizing compounds suitable for the material according to the present invention cannot be classified according to any particular chemical groups. They must simply be sufficiently light-sensitive and they must react with the image-producing pyrazolin-5-ones on exposure to light in such a manner that the image-producing compounds are converted into non-volatile reaction products.

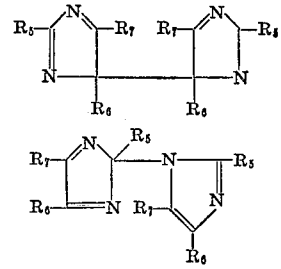
Bis-imidazolyl compounds of the following formula have been found to be especially suitable:



in which R_5, R_6 and R_7 represent an aromatic carbocyclic or heterocyclic group, e.g. a group of the phenyl or naphthyl series, thienyl or the like; the aromatic rings may carry further substituents, e.g. (1) halogen such as fluorine, chlorine or bromine, (2) cyano, (3) alkyl groups which may be substituted e.g. with halogen such as fluorine, chlorine or bromine, nitril, alkoxy or phenyl, (4) alkoxy or alkylthio preferably containing up to 5 carbon atoms, (5) aryloxy or arylthio, especially phenoxy or naphthoxy, (6) alkyl sulfonyl preferably containing up to 5 carbon atoms, (7) aryl sulfonyl, especially phenyl sulfonyl, (8) acyloxy and acylamino groups, e.g. those derived from aromatic or aliphatic carboxylic acids, e.g. benzoyl or acetyl, (9) sulfamoyl or carbamoyl groups which preferably have alkyl or aryl substituents on the N-atom, (10) alkyl and arylamino group preferably containing up to 8 carbon atoms, (11) alkoxy carbonyl and aryloxy carbonyl groups preferably containing up to 8 carbon atoms.

The substituents R_5, R_6 and R_7 may be the same or different and are preferably compounds in which R_5 is an ortho-substituted phenyl group.

Among the various possible positional isomers as regards the connection between the two imidazole rings, the two following isomers are the most suitable on account of their high sensitivity to light:



The bis-imidazolyl derivatives shown in the following table have been found to be especially suitable.

TABLE II

Compound number	R_5	R_6	R_7
1	o-Acetoxyphenyl	Phenyl	Phenyl.
2	o-Benzylphenyl	do	Do.
3	1-Naphthyl	do	Do.
4	do	1-naphthyl	Do.
5	do	p-Methoxyphenyl	p-Methoxyphenyl.
6	2-methoxy-1-naphthyl	Phenyl	Phenyl.
7	3-methoxy-2-naphthyl	do	Do.
8	o-Benzylthiophenyl	o-Benzylthiophenyl	o-Benzylthiophenyl.
9	o-Bromophenyl	Phenyl	Phenyl.
10	do	o-Bromophenyl	Do.
11	do	o-Methoxyphenyl	o-Methoxyphenyl.
12	2-bromo-4-phenyl	Phenyl	Phenyl.
13	o-Butoxyphenyl	do	Do.
14	o-tert.-Butoxyphenyl	do	Do.
15	o-tert.-Butylphenyl	o-tert.-Butylphenyl	o-tert.-Butylphenyl.
16	do	p-tert.-Butylphenyl	p-tert.-Butylphenyl.
17	o-N-butylacetamidophenyl	Phenyl	Phenyl.
18	o-Butylthiophenyl	do	Do.
19	o-Butyryloxyphenyl	do	Do.
20	o-Chlorophenyl	do	Do.
21	do	p-Chlorophenyl	Do.
22	do	3,4-dichlorophenyl	Do.
23	do	m-Pentyloxyphenyl	Do.
24	do	do	m-Pentyloxyphenyl.
25	do	p-Propionyloxyphenyl	Phenyl.
26	2-chloro-4-phenyl	Phenyl	Do.
27	o-Cyanophenyl	do	Do.
28	do	p-tert.-Butylphenyl	Do.
29	do	p-Cyanophenyl	p-Cyanophenyl.
30	do	p-Methoxyphenyl	p-Methoxyphenyl.
31	9-phenanthryl	Phenyl	Phenyl.
32	2,3-dibromophenyl	do	Do.
33	2,4-dibromophenyl	do	Do.
34	2,6-dibutylphenyl	do	Do.
35	2,4-di-tert.-butylphenyl	do	Do.
36	do	2,4-difluorophenyl	Do.
37	do	p-Fluorophenyl	p-Fluorophenyl.
38	o-Dibutylsulfamoylphenyl	Phenyl	Phenyl.
39	2,4-dichlorophenyl	do	Do.
40	do	o-Bromophenyl	Do.
41	2,4-dicyanophenyl	p-Cyanophenyl	p-Cyanophenyl.

TABLE II—Continued

Compound number	R_5	R_6	R_7
42	2,6-dicyanophenyl	Phenyl	Phenyl.
43	2,4-diethoxyphenyl	do	Do.
44	o-Diethylsulfamoylphenyl	do	Do.
45	2,5-difluorophenyl	p-Cyanophenyl	Do.
46	2,3-dimethoxyphenyl	Phenyl	Do.
47	2,4-dimethoxyphenyl	do	Do.
48	do	o-Chlorophenyl	o-Chlorophenyl.
49	do	o-Methoxyphenyl	Phenyl.
50	do	p-Methoxyphenyl	Do.
51	do	m-Phenylthio	m-Phenylthio.
52	o-Dimethylaminophenyl	Phenyl	Phenyl.
53	do	d-Dipentylaminophenyl	Do.
54	do	o-Dipropylsulfamoylphenyl	Do.
55	o-Dimethylcarbamoylphenyl	Phenyl	Do.
56	2,4-dinaphthylthiophenyl	do	Do.
57	2,4-dipentylphenyl	2,4-dipentylphenyl	2,4-dipentylphenyl.
58	do	2-naphthyl	2-naphthyl.
59	o-Dipentylaminophenyl	Phenyl	Phenyl.
60	2,4-dipropoxyphenyl	do	Do.
61	do	o-Diethylcarbamoylphenyl	Do.
62	o-Dipropylcarbamoylphenyl	Phenyl	Do.
63	o-Ethoxyphenyl	do	Do.
64	o-Ethoxycarbonylphenyl	do	Do.
65	o-Ethylphenyl	do	Do.
66	o-N-ethylbutyramidophenyl	do	Do.
67	o-N-ethylpropylaminophenyl	do	Do.
68	o-Ethylthiophenyl	do	Do.
69	o-N-ethylvaleramidophenyl	p-tert.-Pentylphenyl	Do.
70	o-Fluorophenyl	Phenyl	Do.
71	do	o-Methoxyphenyl	o-Methoxyphenyl.
72	o-Methoxyphenyl	Phenyl	Phenyl.
73	do	p-Chlorophenyl	Do.
74	do	p-Methoxyphenyl	Do.
75	do	o-Methylthiophenyl	o-Methylthiophenyl.
76	do	p-Nitrophenyl	Phenyl.
77	do	p-Phenylsulfonylphenyl	p-Phenylsulfonylphenyl.
78	o-Methoxycarbonylphenyl	Phenyl	Phenyl.
79	do	2-naphthyl	Do.
80	do	p-N-Ethylphenylsulfamonlphenyl	Do.
81	4-(2-methoxy-phenyl)-phenyl	Phenyl	Do.
82	o-Methylphenyl	do	Do.
83	do	p-Benzoyloxyphenyl	p-Benzoyloxyphenyl.
84	o-N-methylacetamidophenyl	o-N-ethylbutyramidophenyl	o-N-ethylbutyramidophenyl.
85	do	o-N-methylacetamidophenyl	o-N-methylacetamidophenyl.
86	o-N-methylpropionamidophenyl	Phenyl	Phenyl.
87	o-Methylthiophenyl	do	Do.
88	o-1-naphthylphenyl	o-Phenoxyphenyl	Do.
89	o-2-naphthylphenyl	Phenyl	Do.
90	o-tert.-Pentylphenyl	do	Do.
91	o-Pentyloxyphenyl	do	Do.
92	o-Pentyloxycarbonylphenyl	do	Do.
93	do	2-naphthyl	2-naphthyl.
94	o-9-phenanthrylphenyl	p-Methoxyphenyl	p-Methoxyphenyl.
95	o-Phenoxyphenyl	Phenyl	Phenyl.
96	do	3,4,5-trimethoxyphenyl	3,4,5-trimethoxyphenyl.
97	2-biphenylyl	Phenyl	Phenyl.
98	do	p-Methoxycarbonylphenyl	p-Methoxycarbonylphenyl.
99	do	m-Pentyloxycarbonylphenyl	m-Pentyloxycarbonylphenyl.
100	do	p-Pentyloxycarbonylphenyl	Do.
101	do	4-biphenylyl	4-biphenylyl.
102	o-Phenylthiophenyl	p-1-naphthylthiophenyl	p-1-naphthylthiophenyl.
103	o-Propoxyphenyl	Phenyl	Phenyl.
104	2,4,6-tribromophenyl	do	Do.
105	2,4,6-tributylphenyl	do	Do.
106	2,3,5-trichlorophenyl	do	Do.
107	2,4,6-trichlorophenyl	do	Do.
108	do	o-Butylthiophenyl	Do.
109	2,4,6-tricyanophenyl	p-Cyanophenyl	p-Cyanophenyl.
110	2,4,6-triethoxyphenyl	Phenyl	Phenyl.
111	2,4,6-trimethoxyphenyl	do	Do.
112	2,4,6-tri-tert.-pentylphenyl	do	Do.
113	2,4,6-tripropoxyphenyl	do	Do.
114	p-Chlorophenyl	do	Do.
115	p-Fluorophenyl	do	Do.
116	Phenyl	p-Methoxyphenyl	p-Methoxyphenyl.
117	3,4-dimethoxyphenyl	Phenyl	Phenyl.
118	5-acenaphthylphenyl	do	Do.
119	4-dimethylaminophenyl	do	Do.
120	3-nitrophenyl	do	Do.
121	Phenyl	do	Do.
122	1-naphthyl	1-naphthyl	1-naphthyl.
123	o-Chlorophenyl	o-Chlorophenyl	Phenyl.
124	do	do	o-Chlorophenyl.
125	o-Cyanophenyl	p-tert.-Butylphenyl	p-tert.-Butylphenyl.
126	2,5-difluorophenyl	p-Cyanophenyl	p-Cyanophenyl.
127	2,4-dimethoxyphenyl	o-Chlorophenyl	Phenyl.

The above bis-imidazolyl compounds are prepared by known methods, e.g. those described in Italian Pat. No. 707,086, French Pat. No. 1,351,818, British Pat. No. 997,396 and the publications in J. Org. Chem., 2, 319 (1937) and in Ber., 70, 570 (1937) and the publications by C. S. Hayashi in Bull. Chem. Soc., Japan, 33, 565 (1960).

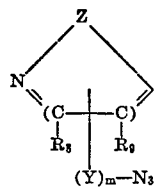
The most advantageous method is the oxidative dimerization of monoimidazolyl compounds in an alkaline organic medium by means of hexacyano ferrate-(III) compounds, e.g. potassium hexacyano ferrate. This process predominantly leads to the formation of bis-imidazolyl compounds in which the two imidazole rings are connected via a C—N bridge (1,2'-bis-imidazoles or C—N isomers), but bis-imidazoles which are connected via a C—C bridge, e.g. 4,4'-bis-imidazoles or other C—C isomers, may also be formed in this process.

It is immaterial whether the bis-imidazoles used according to the invention are present in the C—C or C—N isomeric form or as an isomeric mixture. The important factor is that on exposure they should react with the image-producing pyrazolin-5-one compounds to form non-volatile reaction products.

Organic azides are also suitable for use as light-sensitive photo-oxidizing compounds for the material according to the invention, especially light-sensitive aryl azides

or heterocyclic azides which contain at least one azido group which may be directly attached to the aromatic ring or connected to it via a carbonyl or sulfonyl group. The light-sensitive azido compounds may be monomers or polymers. The choice of light-sensitive azido compound will depend on the requirements of the particular reproduction process. The most suitable azides for a particular process can be determined by the conventional tests used in the art.

Heterocyclic azides of the following general formula have proved to be particularly suitable:



In the above formula

Z represents the ring members required to complete a 5-membered or 6-membered heterocyclic ring which contains nitrogen, e.g. an oxazole, thiazole, selenazole, imidazole, pyridine, pyrrole or pyrimidine ring, or the condensed heterocyclic rings resulting from condensation of the above with an aromatic ring system;

Y is an arylene group, preferably phenylene or a phenylene-carbonyl methylene group in which the phenylene rings may contain further substituents such as alkyl or alkoxy, both of which preferably contain up to 3 carbon atoms, hydroxyl, halogen such as fluorine, chlorine or bromine or the like;

R_8, R_9 can be the same or different and stand for (1) hydrogen, (2) saturated or olefinically unsaturated aliphatic groups having preferably up to 5 carbon atoms, (3) aryl, especially phenyl, (4) amino which may be substituted with alkyl or acyl, (5) halogen such as chlorine or bromine, (6) hydroxyl, (7) alkoxy preferably having up to 5 carbon atoms, (8) carboxyl, (9) esterified carboxyl, especially with aliphatic alcohols, (10) carbamoyl, (11) sulfo, (12) sulfamoyl or (13) cyano;

R_8 and R_9 also represent the ring members required to complete a condensed benzene or naphthalene ring;

m=0 or 1; and

n=0 or 1.

Light-sensitive compounds of the 9-azido-2,3-benzacridine, 4-azidoquinoline or 9-azidoacridine series are preferred. The compounds have the same basic structure. They differ from each other merely by a condensed benzene ring. Substitution products of these basic compounds may also be used, e.g. those which are substituted with alkyl preferably containing up to 6 carbon atoms such as methyl, ethyl, propyl or butyl, or alkoxy which also preferably contains up to 6 carbon atoms, amino or mono- or di-alkyl-amino also preferably containing up to 6 carbon atoms in the alkyl group, halogen such as chlorine or bromine, nitro, cyano, carboxyl or esterified carboxyl group.s

Phenyl azides, naphthyl azides, phenyl carbonyl azides, naphthyl carbonyl azides, phenyl sulfonyl azides and naphthyl sulfonyl azides are also suitable. Aryl azides in which two phenyl or naphthyl rings are conjugated to each other by one or more vinylene groups have been found to be particularly suitable, e.g. stilbenazides. In these compounds, the chain consisting of vinylene groups may be interrupted by carbonyl groups.

Suitable azides are shown in Table III below.

TABLE III

(1) p-methoxybenzene sulfazide
(2) fluorenone-2,7-disulfazide (decomposition 161 to 162° C.)
(3) 2,3-diazidonaphthoquinone-(1,4)
(4) 2,4-diazido-6-methyl pyrimidine
(5) 2-azidobenzoxazole
(6) 2-azidobenzothiazole
(7) 2-azidomethylene-3-ethyl rhodanine (M.P. 108–109° C.)
(8) 2-azidomethylene-3-phenyl rhodanine (M.P. 119–121° C.)
(9) 4-azidoquinoline
(10 4-azidoquinaldine
(11) 2-methyl-3-phenyl-4-azidoquinoline
(12) 4-azido-7-nitroquinoline
(13 2-methyl-4-azido-7-dimethylaminoquinoline
(14) 9-azidoacridine
(15) 2-chloro-9-azidoacridine
(16) 2-methoxy-6-chloro-9-azidoacridine
(17) 2-methyl-9-azidoacridine
(18) 2-nitro-9-azidoacridine
(19) 3-dimethylamino-9-azidoacridine
(20) 9-azido-2,3-benzacridine
(21) 9-azido-3,4-benzacridine
(22) 9-azido-4-carbamoylacridine (decomposition 230° C.)
(23) 9-azido-2-carbethoxyaminoacridine (M.P. 172° C.)
(24) 9-azido-1,2,3,4-tetrahydroacridine
(25) 2,6-diphenyl-4-azido pyrimidine
(26) 1,4-bis-[2-(4-azidobenzoyl)-vinyl]-benzene
(27) bis-[4-azidostyryl]-ketone
(28) 2,5-bis-[4-azidobenzylidene]-cyclopentanone
(29) 2,5-bis-[4-azidobenzylidene]-2,5-dihydrothiophene-S-dioxide
(30) 2,6-bis-[3-azidobenzylidene]-cyclohexanone (M.P. 80–85° C.)
(31) [3-azidostyryl]-[4-azidophenyl]-ketone (M.P. 86–88° C.)
(32) 4-azidocinnamic acid anilide
(33) 1,6-bis-[4-azidophenyl]-hexatriene-(1,3,5)
(34) 4-azidobenzophenone
(35) 2,6-bis-[4-azido-γ-chlorocinnamylidene]-cyclohexanone (decomposition 140 to 148° C.)
(36) 1,2-bis-[4-azidobenzoyl]-ethylene (decomposition 136° C.)
(37) 2,6-bis-[4-azidobenzylidene]-cyclohexanone
(38) 2-[4-azidobenzoyl methylene]-α-naphthothiazol
(39) 2-p-tosylamino-9-azidoacridine (decomposition 102–104° C.)
(40) 2-benzoylamino-9-azidoacridine (decomposition 108–111° C.)

The azides mentioned above are prepared by known methods, for example compounds (1) to (25), (39) and (40) by reacting the corresponding halogen compounds with sodium azide (as described, for example, in German Offenlegungsschrift No. 1,547,774) and compounds (26) to (38) by the condensation of aldehydes with active methylene compounds. Another suitable process for their preparation is the Sandmeyer reaction.

The materials according to the invention preferably contain the image-producing pyrazolin-5-one compounds and the light-sensitive compounds in a molar ratio of about 1:1 to 6.

The light-sensitive layers contain the light-sensitive compounds, e.g. at least one of the light-sensitive azides, in quantities of 0.1 to 1.5 g./m.² and one or more image-producing pyrazolin-5-one compounds in quantities of 0.03 to 0.6 g./m.² or at least one of the light-sensitive bis-imidazoles in quantities of 0.5 to 8 g./m.² and one or more image-producing pyrazolin-5-one compounds in quantities of 0.1 to 1.5 g./m.². These ranges of concentration have been found to be suitable, although concentrations outside these ranges may, of course, be employed.

The concentration depends mainly on the requirements of the particular reproduction process.

To prepare the light-sensitive layer, the light-sensitive compound and the image-producing compound may be dissolved or suspended in solvents, mixed with a binder and applied to the layer support.

Suitable binders for the light-sensitive layer are the usual natural or synthetic film-forming polymers, e.g. proteins, especially gelatine, cellulose derivatives, especially cellulose ethers, cellulose esters or carboxymethyl cellulose, alginic acid and its derivatives, starch ether or galactomannan, polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl chloride, copolymers of vinyl chloride and vinyl acetate, polyvinyl acetate or partly saponified polyvinyl acetate or copolymers of vinyl acetate, copolymers of acrylonitrile and acrylamide, polyacrylic acid esters, polymethacrylic acid esters, polyethylene, etc. The light-sensitive layers may either be used as self-supporting layers or applied to a layer support. Suitable layer supports are e.g. paper, especially baryta paper or backed paper, cellulose esters, e.g. cellulose triacetate, polyesters, especially those based on ethylene terephthalate, glass, etc.

The image-receiving material preferably consists of an image-receiving layer applied to a suitable layer support. Substantially the same substances as those described above for the light-sensitive materials may be used both as binder for the image-receiving layer and as layer support.

When choosing the binder for the light-sensitive layer and the image-receiving layer, it must be kept in mind that the layers must not become sticky in the heat. These difficulties, however, are well known from other transfer processes such as the silver salt diffusion process or the heat development process and can easily be solved on the basis of the methods used in these known fields.

The image-receiving layer contains compounds which should be substantially insensitive to visible light under the conditions of the process of the invention and which must react with transferred image-producing compounds to form colored products. Numerous compounds have been found to be suitable for this purpose. Chemically, these compounds belong to many different classes so that they cannot be definitely classified on a chemical basis, but suitable compounds and suitable combinations of an image-producing compound for use in the light-sensitive layer and of its reactant which is used in the image-receiving layer to produce the reaction which yields the image dye can easily be identified by a few simple laboratory tests. Thus the two reactants must react to produce a stable image dye when heated for a few seconds to a temperature of between about 80° C. and 200° C. A second test is then necessary to choose suitable image-producing compounds. This test should indicate whether the image-producing compound reacts sufficiently rapidly with the light-sensitive azide or bis-imidazole on exposure to light so that when the exposed mixture is heated in the presence of the reactant in the image-receiving layer it will no longer yield a colored compound.

Compounds in the following classes of compounds are examples of suitable reactants in the image-receiving layer for the image-producing pyrazolin-5-one compounds:

(1) Noble metal compounds, e.g. compounds of silver, gold or platinum. Suitable examples are the salts of these metals with long-chain aliphatic carboxylic acids, having preferably between 6 and 30 carbon atoms. Silver compounds which are largely insensitive to light under the conditions of the copying process carried out according to the invention have been found to be particularly suitable, e.g. the silver salts of aliphatic carboxylic acids having a thioether group as described in British Pat. No. 1,111,492 or silver salts of long-chain fatty acids, such as silver behenate, silver palmitate, silver stearate, etc.

When the above mentioned noble metal compounds are used, the copies obtained are generally brown to black. The image consists of the metal and/or a reaction product of the transferred image-producing compound.

(2) Diazonium salts which react with the transferred pyrazolin-5-one compound via the hydrogen atom in the 4-position of the pyrazoline ring to form a colored product. This reaction is similar in principle to the reaction employed in the known diazo-type photographic process.

(3) Compounds which react in their oxidised form with pyrazolin-5-one under oxidising conditions to form colored coupling products. Suitable reactants are e.g. the oxidation products of p-phenylene diamines or their derivatives which react with the pyrazolin-5-one compounds to form azomethine dyes of the type known in color photography.

In addition to the image-forming reactants properly speaking, the image-receiving layers may also contain additives which have an advantageous influence on the color tone, contrast, stability, etc. of the copy. Image-receiving layers of this type are already known and have been described for example in German Pats. Nos. 895,101 and 1,003,577 and in Belgian Pats. Nos. 614,064 and 609,057.

The image-receiving layers may also contain white pigments such as zinc oxide, silicon dioxide or titanium dioxide as fillers for improving the whites and to control the tendency of the layers to stick, and they may contain terpene resins and organic acids to improve the stability in storage. Image-receiving layers of this type have been described in U.S. Pats. Nos. 3,074,809 and 3,107,174.

The color tone of the resulting images may be improved e.g. by addition of compounds of the 1-(2H)-phthalazinone series. Toners of this type have been described in U.S. Pats. Nos. 3,080,254 and 3,446,648. Additives which accelerate the reduction reaction in the image-receiving layer have also been found to be advantageous. Sterically hindered phenols, e.g. 2,6-di-tert-butyl - p - cresol, are suitable for this purpose, for example. Compounds of this type have been described in U.S. Pat. No. 3,218,166. The image tone and density can also be improved by certain metal salts, e.g. copper-II stearate. Ionic metal compounds of this type which intensify the image and their use have been described in German Auslegeschrift No. 1,572,209.

The light-sensitive layers according to the invention may be exposed to the usual sources of light used in reproduction work, e.g. mercury vapour lamps, iodine quartz lamps or incandescent lamps. The spectral sensitivity of the light-sensitive material depends on the nature of the azides and bis-imidazoles used.

Exposure may be carried out either in contact or optically or in reflex position.

Transfer of the image-producing compounds from the unexposed areas of the light-sensitive layers to the image-receiving layer is carried out in the heat at temperatures of between 80° C. and 200° C. The layers may be heated e.g. by passing the exposed light-sensitive layer over hot plates or rollers in contact with the image-receiving layer or by irradiation with infra-red light. The best temperature and heating time depend, of course, on the nature of the compound which is to be produced, and can easily be determined by a few simple tests.

The spectral sensitivity of the light-sensitive materials depends on the nature of these materials. The bis-imidazole compounds used according to the invention, for example, are generally sensitive to wavelengths below 300 nm. of the ultraviolet portion of the spectrum. The organic azido compounds are generally also sensitive to the ultraviolet part of the spectrum, whereas the 9-azido-acridines are already sensitive to the part of the spectrum ranging from blue to green, in the region of about 350 to 540 nm.

A special advantage of the light-sensitive system for use according to the invention, which consists of the bis-imidazole or organic azide and the image-producing compound, is that the system can be optically sensitized.

Practically any compounds used for the optical sensitization of silver halide emulsions are suitable for use as sensitisers for the material according to the invention; this means especially cyanine dyes, merocyanines, oxonoles, rhodacyanines or various types of styrly com-

pounds, e.g. as described in the book by F. M. Hamer, "The Cyanine Dyes and Related Compounds" (1964).

The nitrile substituted thioamide sensitizers described in French Pat. No. 1,574,890 or U.S. application Ser. No. 727,696, now U.S. Pat. No. 3,617,296, and their homologues such as the corresponding tetramethine compounds are also suitable.

The technique used for sensitizing is also similar to that commonly used in silver halide photography. The sensitizers are dissolved in a suitable solvent such as short-chain aliphatic alcohols or aqueous systems and added to the layers before casting. The concentration of optical sensitizers may vary within wide limits. Quantities of between 1 and 10 g. per mol of light-sensitive compounds have generally been found to be sufficient but larger quantities may in some cases be necessary, e.g. in the case of dyes which have a low extinction.

The most suitable sensitizers for any given system can easily be determined by the usual sensitometric tests which are commonly used in silver halide photography.

The addition of sensitizers results not only in an increase in the range of spectral sensitivity but also in a considerable increase in the overall sensitivity, which is especially desirable for obtaining short copying times. Owing to the possibility of sensitizing the layers according to the invention, perfect copies of colored originals can be obtained.

According to one modification of the material according to the invention, the image-receiving layer and the light-sensitive layer may be combined on one support. In this case, a transparent layer support must be used, and the image-receiving layer, e.g. a layer containing silver behenate and behenic acid (molar ratio 1:1) dispersed in a copolymer of styrene and isobutylene, is applied first to the support and the light-sensitive layer, e.g. a layer of ethyl cellulose containing the light-sensitive compound and the pyrazolin-5-one, is then applied to the image-receiving layer.

EXAMPLE 1

Light-sensitive material

The following casting solution is applied in a quantity of 35 g./m.² to a layer support of pergamin paper:

10 g. of bis-[2-(2,4-dichlorophenyl) - 4,5 - diphenyl-imidazole],
1 g. of N-(2,5-dichlorophenyl)-3-methyl-pyrazolin-5-one,
10 g. of ethyl cellulose, and
500 ml. of butanone-2.

The layer is dried in the usual manner.

The image-receiving material is prepared by grinding up:

2.1 g. of a mixture of silver behenate and behenic acid (molar ratio 1:1),
1.66 g. of terpene resin,
0.86 g. of 1-(2H)-phthalazinone,
4.8 g. of zinc oxide,
0.56 g. of silica gel,
0.37 g. of 2,6-di-tert-butyl-4-methyl phenol,
0.034 g. of tetrachlorophthalic acid anhydride,
15 g. of an 8% solution of ethyl methacrylate in pentanone-3,
80 g. of a 1.5% polyvinyl acetate solution in butyl acetate, and
30 g. of butyl acetate,

for 6 hours in a ball mill and then applying the mixture to paper and drying it.

The dried layer contains about 0.2 g. of silver per m.² in the form of the above silver salt.

Processing

The light-sensitive material is exposed to a 1000 watt source of UV light from a distance of 5 cm. through a positive transparent original for 3 seconds.

The exposed layer is then brought into contact with the image-receiving layer and heated to a temperature of 125° C. for 5 seconds.

A sharp, deep black positive copy of the transparent original is obtained.

If the sensitising dye 2-(4-dimethylaminostyryl)-benzothiazole is added to the casting solution for the light-sensitive layer in an amount of 1 g. per 500 ml., the imagewise exposure may be carried out with an ordinary incandescent lamp (tungsten filament).

If the tungsten filament lamp has a power of 1500 watt, the exposure time at the same distance between light-sensitive material and source of light is 30 seconds. Subsequent processing is identical. A deep black copy of equally good quality is obtained.

Instead of a transparent copy, a text printed on ordinary paper may be used as original copy. Exposure must in this case be carried out in reflex position. The exposure times are between 15 to 25 seconds under otherwise the same conditions.

Similar results may also be obtained with other pyrazolin-5-one compounds, e.g. 1-phenyl-3-methyl pyrazolin-5-one.

EXAMPLE 2

Light-sensitive material

The light-sensitive material used is the same as in Example 1 except that the pyrazolin-5-one compound contained in it is 1-phenyl-3-methyl-pyrazolin-5-one used in the same quantity.

Image-receiving layer

The following casting solution is applied to a layer support of baryta paper:

5 g. of 4-dimethylaminobenzene diazonium tetrafluoroborate,
1 g. of saponine,
1 g. of polyoxyethylene hydroxyethyl cellulose,
100 ml. of water.

Processing

The material is processed as described in Example 1. A red positive image of the original is obtained on a grey background.

EXAMPLE 3

Light-sensitive material

The following casting solution is applied in a quantity of 25 g. per m.² to a layer support of pergamin paper:

15 g. of bis-[2-(2-chlorophenyl)-4,5-diphenyl-imidazole],
1 g. of N-(2,5-dichlorophenyl)-3-methyl-pyrazolin-5-one,
10 g. of ethyl cellulose,
400 ml. of butanone-2.

Processing

The material is exposed for 30 seconds to the reflected light of an ordinary 1500 watt incandescent lamp. The image-receiving material described in Example 1 is used. Processing is carried out in the same way. A sharp dark brown image of the original is obtained.

EXAMPLE 4

Light-sensitive material

A light-sensitive layer is prepared by dissolving one of the combinations of an azido compound with a pyrazolin-5-one mentioned in Table IV below in the given proportions in 10 ml. of butanone-2, adding 5 ml. of 5% ethyl cellulose in butanone-2, and applying the solution to a support and drying.

TABLE IV

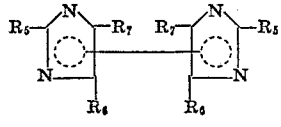
Quantity (mg.)	Azide number	Quantity (mg.)	Pyrazolin-5-one number
30	40	10	7
60	39	20	5
30	14	15	20
60	39	40	33
60	39	20	26
60	39	10	4
60	39	30	20
60	39	15	8
60	39	30	24
60	39	15	3
30	14	15	3
30	14	15	26
30	14	15	33
30	10	10	7
30	20	10	7
30	27	10	7
60	34	10	4
60	37	5	5
60	31	10	5
60	32	10	5
60	6	20	33
60	6	10	7
60	6	20	26

Processing

The light-sensitive layer is exposed to a 75 watt mercury vapour lamp at a distance of 20 cm. through an original copy for 2 minutes and then heated to a temperature of 125° C. to 140° C. for 5 to 10 seconds in contact with the image-receiving material of Example 1. Brown to brownish-black copies of the original are obtained. When azides of the acridine series are used in the light-sensitive layer, iodine quartz lamps or incandescent lamps may be used as the sources of light.

What is claimed is:

1. In a process for the production of copies including the steps of image-wise exposing a light-sensitive layer which contains a light-sensitive photooxidizing compound and an image-producing compound capable of being transferred to an image-receiving layer, the image-producing compound in the exposed areas being converted into a non-transferable compound by reaction with the light-sensitive compound, bringing the exposed layer into contact with an image-receiving layer which contains compounds which react with the image-producing compound to form colored compounds and heating of the layers while in contact with each other to a temperature at which the image-producing compound is transferred from the unexposed areas of the light-sensitive layer to the image-receiving layer, the improvement consisting of exposing a light-sensitive layer which contains a light-sensitive photooxidizing compound selected from the group consisting of heterocyclic azide, aryl azide, carbonyl azide, sulfonyl azide, and bis-imidazole of the following formula:

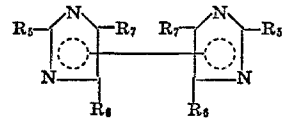


in which

R_5, R_6 or R_7 represent a group of the naphthyl or phenyl series,

and a pyrazolin-5-one which contains at least one hydrogen atom or a 4-aminophenylamino group in the 4-position of the pyrazolone ring, said pyrazolin-5-one compound being transferable at a temperature of between 80° C. and 200° C.

2. In a light-sensitive photographic composition containing a light-sensitive photooxidans as an oxidizing agent and an image-producing compound that is transferable at least one hydrogen atom or one 4-amino-phenylamino composition is heated, the light-sensitive compound in the exposed areas being capable of reacting with the image-producing compound to form a non-transferable reaction product, the improvement according to which the image-producing compound is a pyrazolin-5-one which contains at least one hydrogen atom or one 4-amino-phenylamino group in the 4-position of the pyrazolone ring, and the light-sensitive photooxidans is selected from the group consisting of heterocyclic azide, aryl azide, carbonyl azide, sulfonyl azide, and bis-imidazole of the following formula:

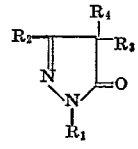


in which

R_5, R_6 or R_7 represent a group or the naphthyl or phenyl series,

and a pyrazolin-5-one being transferable at a temperature of between 80° C. and 200° C.

3. The process of claim **1**, wherein the light-sensitive material contains, as image-producing, transferable compound, a pyrazolin-5-one derivative of the following formula:



in which

R_1 is (1) hydrogen, (2) a saturated or an olefinically unsaturated aliphatic group, (3) aryl, (4) a heterocyclic group, or (5) cycloalkyl;

R_2 is (1) hydrogen, (2) a saturated or an olefinically unsaturated aliphatic group, (3) aryl, (4) a heterocyclic group, (5) cycloalkyl, (6) hydroxyl, (7) alkoxy, (8) an amino group, or (9) an alkoxy carbonyl group;

R_3 is (1) hydrogen, (2) a saturated or an olefinically unsaturated aliphatic group, (3) aryl, (4) an amino group, or (5) alkoxy;

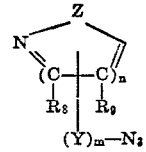
R_4 is hydrogen or a 4-aminophenylamino group;

R_2 and R_3 may also represent the ring members required to complete a 5- or 6-membered carbocyclic or heterocyclic ring.

4. The process of claim **1**, wherein the light-sensitive azide is an azide of the 9-azidoacridine, 9-azido-2,3-benzacridine or 4-azidoquinoline series.

5. The process of claim **1**, wherein the bis-imidazole contains an ortho-substituted phenyl radical in the 2-position.

6. The process of claim **1**, wherein the light-sensitive material contains, as light-sensitive compounds, a heterocyclic azide of the following formula:



in which

Z represents the ring members required to complete a 5-membered or 6-membered heterocyclic ring which contains nitrogen;

Y is an arylene group;

R_8 or R_9 represent hydrogen, a saturated or an olefinically unsaturated aliphatic group, aryl, an amino group, halogen, hydroxyl, alkoxy, carboxyl, esterified carboxyl, carbamoyl, sulfo, sulfamoyl or cyano;

R_8 and R_9 may also represent the ring members required to complete a condensed benzene or naphthalene ring;

m is 0 or 1; and

n is 0 or 1.

7. The process of claim 1, wherein the light-sensitive layer contains a merocyanine, a styryl dye or another polymethine sensitizer.

8. The process of claim 1, wherein the image-receiving layer contains heavy metal compounds which are not light-sensitive under the conditions of the process.

9. The process of claim 8, wherein the image-receiving layer contains a silver compound which is insensitive or almost insensitive to light under the conditions of the process.

10. The process of claim 9, wherein the image-receiving layer contains silver salts of a long-chain aliphatic carboxylic acid having 8 to 24 carbon atoms.

11. The process of claim 9, wherein the image-receiving layer contains a silver salt of an aliphatic carboxylic acid which is substituted with a thioether group.

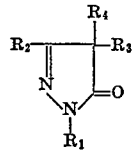
12. The process of claim 8, wherein the image-receiving layer contains a toner.

13. The process of claim 8, wherein the image-receiving layer contains a sterically hindered phenol.

14. The process of claim 8, wherein the image-receiving layer contains a white pigment.

15. The process of claim 8, wherein the image-receiving layer contains a terpene resin.

16. The photographic material of claim 2, wherein the pyrazolin-5-one has the following formula:



in which

R_1 is (1) hydrogen, (2) a saturated or an olefinically unsaturated aliphatic group, (3) aryl, (4) a heterocyclic group, or (5) cycloalkyl;

R_2 is (1) hydrogen, (2) a saturated or an olefinically unsaturated aliphatic group, (3) aryl, (4) a heterocyclic group, (5) cycloalkyl, (6) hydroxyl, (7) alkoxy, (8) an amino group, or (9) alkoxy carbonyl;

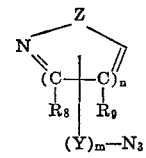
R_3 is (1) hydrogen, (2) a saturated or an olefinically unsaturated aliphatic group, (3) aryl, (4) an amino group, or (5) alkoxy;

R_4 is hydrogen or a 4-aminophenylamino group;

R_2 and R_3 may also represent the ring members required to complete a 5- or 6-membered carbocyclic or heterocyclic ring.

17. The light-sensitive material of claim 2, which contains an azide of the 9-azidoacridine, 9-azido-2,3-benzacridine or 4-azidoquinoline series.

18. The light-sensitive material of claim 2, which contains a light-sensitive azide of the following formula:



in which

Z represents the ring members required to complete a 5-membered or 6-membered heterocyclic ring which contains nitrogen;

Y is an arylene group;

R_8 or R_9 stand for hydrogon, a saturated or an olefinically unsaturated aliphatic group, aryl, an amino group, halogen, hydroxyl, alkoxy, carboxyl, esterified carboxyl, carbamoyl, sulfo, sulfamoyl or cyano;

R_8 and R_9 may be ring members required to complete a condensed benzene or naphthalene ring;

m is 0 or 1; and

n is 0 or 1.

19. The light-sensitive material of claim 2 wherein the bis-imidazole contains an ortho-substituted phenyl radical in the 2-position.

20. The light-sensitive material of claim 2, wherein the light-sensitive layer contains a merocyanine, a styryl dye or another polymethine sensitizer.

References Cited

FOREIGN PATENTS

997,396 7/1965 Great Britain ------ 96—90 PC

NORMAN G. TORCHIN, Primary Examiner

A. T. SURO PICO, Assistant Examiner

U.S. Cl. X.R.

96—27 R, 29 R, 48 HD, 74, 90 PC

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,728,115 Dated April 17, 1973

Inventor(s) Poot et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 15, in claim 2, line 70, cancel "least one hydrogen atom or one 4-amino-phenylamino" and insert -- temperature of between 80°C and 200°C when the -- .

Signed and sealed this 9th day of April 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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