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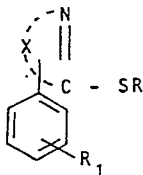
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Photographic products, diffusion transfer photographic process, and compounds used therefor.

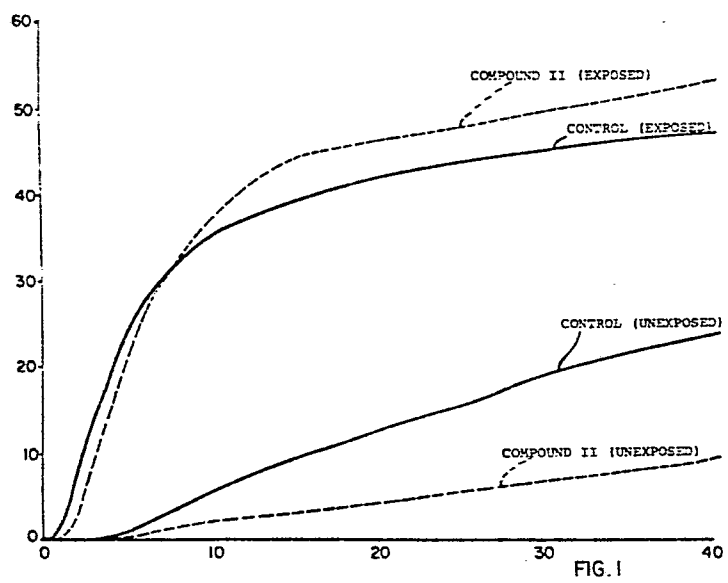
There is disclosed a diffusion transfer photographic system wherein development of an exposed photosensitive element with an aqueous alkaline processing composition is effected in the presence of a compound represented by the formula



wherein X represents the nonmetallic atoms necessary to form a nucleus which completes a 5- or 6-membered heterocyclic moiety on said structure including substituted rings and fused rings; R is H, an alkali metal or a group which is cleavable in a photographic aqueous alkaline processing composition; and R₁ is either a group which has a pK_a of from about 7 to about 14 which is ionizable to an anion whereby the silver salt of the mercaptan (resulting from cleavage or ionization of -SR) is rendered more soluble in the pH range within which R₁ is ionized to an anion than it is below that pH range, or a precursor of such a group.

EP 0 055 858 A2

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European Patent
Application

1 PHOTOGRAPHIC PRODUCTS, DIFFUSION TRANSFER
PHOTOGRAPHIC PROCESS, AND COMPOUNDS USED THEREFOR

5 BACKGROUND OF THE INVENTION

This application relates generally to photography and, more specifically, to diffusion transfer photographic systems including products and processes.

10

Diffusion transfer photographic systems wherein images are formed in colour by the use of image dye-providing materials such as dye developers are well known in the art. Generally, multicolour transfer images are formed by
15 processing an exposed multicolour photosensitive silver halide element with an aqueous alkaline processing composition distributed between two sheet-like elements, one of these elements including an image receiving layer. The processing composition is so applied and confined within
20 and between the two sheet-like elements as not to contact or wet outer surfaces of the two superposed elements, thus providing a film unit whose external surfaces are dry. The processing composition preferably is distributed in
viscous form from a pressure rupturable container.

25

It is known in the art to carry out development in the presence of development restrainers whereby development of exposed silver halide is continued for a period of time sufficient to form an imagewise distribution of diffusible
30 unoxidized dye developers in undeveloped areas of the

1 silver halide emulsion layer(s) with the unoxidized dye
developers being transferred by diffusion to a superposed
image receiving element and, after the predetermined
development period, restraining further development of
5 exposed silver halide by means of the development
restrainer. See, for example, U.S. Patent 3,265,498.
Various development restrainers which are useful for such
purposes are known including mercaptoazoles such as
1-phenyl-5-mercaptotetrazole. However, the use of such
10 development restrainers is subject to certain limitations.
For example, U.S. Patent 3,260,597 discloses that mercapto-
azole development restrainers or "arrestors", such as
1-phenyl-5-mercaptotetrazole, can not be used in the
aqueous alkaline processing composition in any appreciable
15 amount because development of exposed silver halide will be
stopped prematurely particularly in the outer blue and
green sensitive emulsion layers of a multicolour system.

It is also known in the art to use blocked development
20 restrainers which are designed to provide a timed release
of a development restrainer during the development process.
See, for example, U.S. Patent 3,698,898 which discloses
the use of quinone- or naphthoquinone-methide precursors
which release a photographic reagent such as 1-phenyl-5-
25 mercaptotetrazole in the presence of alkali; U.S. patent
4,009,029 which discloses a class of cyanoethyl-containing
blocked development restrainers; German Offenlegungsschrift
2,427,183 which discloses various blocked development
restrainers, and U.S. Patents 3,260,597 and 3,265,498,
30 referred to above, which disclose hydrolyzable blocked
restrainers.

The use of phenylmercaptotetrazole compounds which are
substituted on the phenylring as development inhibitors in
35 certain conventional photographic systems is also known.

1 See, for example, Research Disclosure, July 1974, page 12,
and U.S. Patent 3,295,976.

SUMMARY OF THE INVENTION

5

The present application relates to a diffusion transfer photographic system wherein the development process is carried out in the presence of phenylmercaptoazoles which are substituted on the phenyl ring.

10

It is therefore an object of this invention to provide a novel diffusion transfer photographic system.

15 It is another object to provide a diffusion transfer photographic system wherein development of an exposed photosensitive element is carried out in the presence of phenylmercaptoazole compounds which are substituted on the phenyl ring.

20 It is a further object to provide such a diffusion transfer photographic system wherein the compounds utilized include a blocking group designed to provide a timed release of the substituted phenylmercaptoazoles during the development process.

25

Yet another object is to provide a diffusion transfer photographic process wherein the pH of the processing composition initially is substantially equal to or greater than the pKa of the substituent on the phenyl ring of the phenylmercaptoazole compound and subsequently, during
30 development, the pH is lowered below the pKa.

35 Still another object is to provide a diffusion transfer photographic system wherein the substituted phenylmercaptoazole compounds may be incorporated in the

1 aqueous alkaline processing composition.

A further object is to provide a diffusion transfer
 photographic system wherein the substituted phenylmercapto-
 5 tetrazole compounds may be incorporated in the photo-
 sensitive element.

Yet another object is to provide a diffusion transfer
 photographic system wherein the photographic speed of one
 10 or more silver halide emulsions may be increased.

A still further object is to provide a diffusion transfer
 photographic system wherein fog development may be
 decreased.

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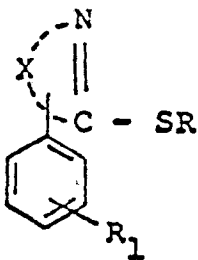
Another object is to provide novel colour diffusion trans-
 fer photographic products and process.

BRIEF SUMMARY OF THE INVENTION

20

These and other objects and advantages are accomplished
 in accordance with the invention by providing a diffusion
 transfer photographic system wherein development of an
 exposed photosensitive element with an aqueous alkaline
 25 processing composition is carried out in the presence of
 compounds which are represented by the formula

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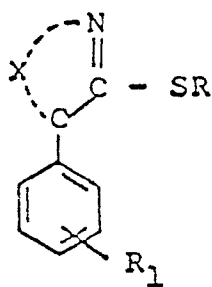
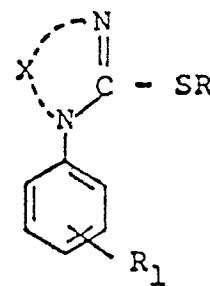
FORMULA A

35

1 wherein X represents the nonmetallic atoms necessary to
 form a nucleus which completes a 5- or 6-membered hetero-
 cyclic moiety on said structure including substituted rings
 and fused rings; R is H, an alkali metal or a group which
 5 is cleavable in a photographic aqueous alkaline processing
 composition; and R₁ is either a group which has a pKa of
 from about 7 to about 14 which is ionizable to an anion,
 preferably about 8.5 or above, whereby the silver salt of
 the mercaptan (resulting from cleavage or ionization of -SR)
 10 is rendered more soluble in the pH range within which R₁
 is ionized to an anion than it is below that pH range, or
 a precursor of such a group.

The compounds which are useful according to the invention
 15 are generally phenylmercaptoazoles wherein the substituted
 phenyl moiety is attached to either a nitrogen atom or a
 carbon atom of the azole moiety. Accordingly, the compounds
 may be represented by either of the following formulas
 which are both within generic Formula A.

20

FORMULA BFORMULA C

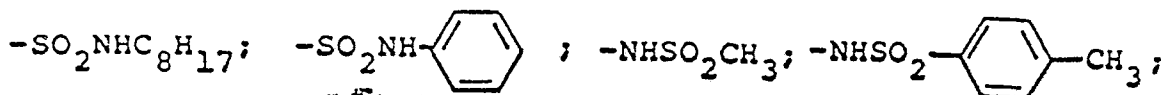
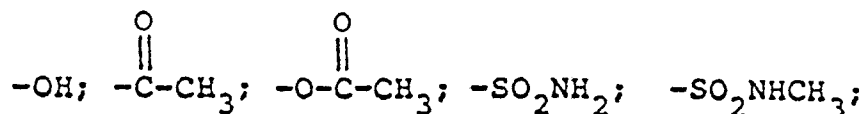
25
 30 The heterocyclic moieties formed by X preferably include
 those wherein the heterocyclic atoms (i.e., atoms other
 than carbon) are members of a single heterocyclic ring as
 contrasted with compounds containing fused or condensed
 heterocyclic rings in which the heterocyclic atoms are
 35 members of more than one heterocyclic ring. Typical

1 suitable compounds include monoazoles such as benzoxazoles,
 benzothiazoles, etc.; diazoles such as benzimidazoles; tri-
 azoles such as 1,2,4-triazoles, etc.; tetrazoles and pyrim-
 idines. In a preferred embodiment of the invention the
 compounds include a tetrazole nucleus.

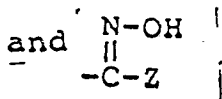
5

The substituent (R_1) on the phenyl moiety may be either
 any suitable substituent which has a pKa of from about
 7 to about 14 which is ionizable to an anion whereby the
 silver salt of the mercaptan (resulting from cleavage or
 10 ionization of $-SR$) is rendered more soluble in the pH
 range within which R_1 is ionized to an anion than it is
 below that pH range, or a precursor of such a substituent.
 Typical suitable substituents are:

15

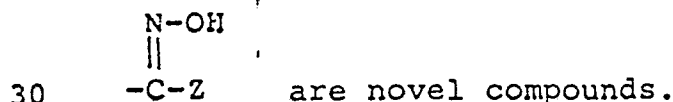


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where Z is H, alkyl having from 1 to 10 carbon atoms,
 aralkyl such as benzyl or phenethyl, phenyl or substituted
 25 phenyl.

The compounds within generic formula A wherein R_1 is



As stated previously, the compounds may include a mercaptan
 group attached to a carbon atom of the azole nucleus or
 may include a blocking group attached to the sulfur atom
 35 with the blocking group designed to cleave from the

1 molecule in an aqueous alkaline medium to provide a timed
 release of the desired phenylmercaptoazole compound. Where
 R is a blocking group it may be any suitable blocking group
 such as, for example, those which cleave by hydrolysis;
 those which cleave by quinone methide elimination (e.g.,

5

R is $-\text{CH}_2-\text{C}_6\text{H}_4-\text{OH}$) such as disclosed in U.S. Patent

3,698,898; those which cleave by hydrolysis followed by
 quinone methide elimination (e.g., R is

10

$-\text{CH}_2-\text{C}_6\text{H}_4-\text{O}-\text{C}(=\text{O})-\text{CH}_3$); and those which cleave by β -elimination

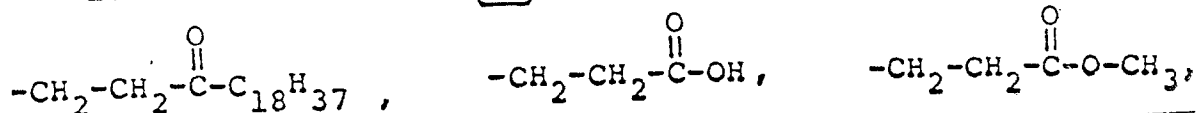
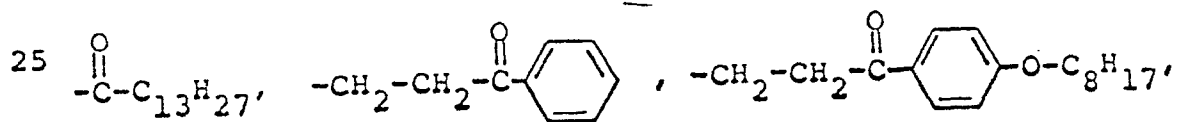
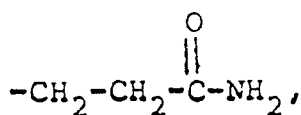
(e.g. R is $\text{CH}_2-\text{CH}_2-\text{CN}$,

15

$-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{R}_2$, $-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{OR}_2$, where R_2 is alkyl, and

$-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{N}(\text{R}_3)(\text{R}_4)$ where R_3 and R_4 are H or alkyl). Typical

20 suitable blocking groups include, for example,

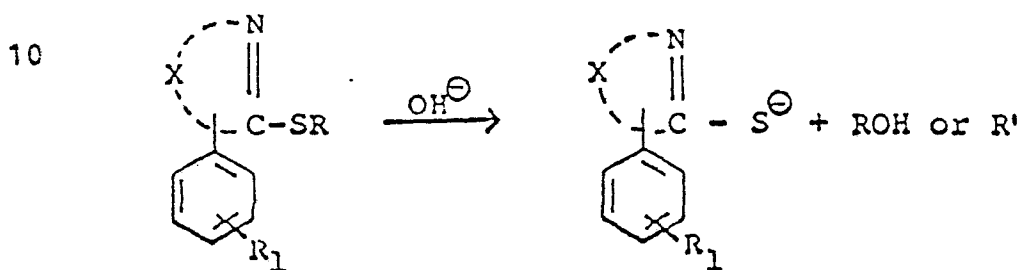


30 and succinimido groups which are substituted on the
 nitrogen atom with alkyl or aryl as disclosed in U.S.
 patent 3,888,677.

35

- 1 In a preferred embodiment of the invention, R is
 -CH₂, -CH₃, SO₂, R₅ where R₅ is alkyl, aryl or substituted aryl.

Cleavage of the blocking group in aqueous alkaline medium
 releases, in a timed fashion during development, the
 5 substituted phenylmercaptoazole moiety. Cleavage of the
 blocking group occurs according to the following reaction
 sequence:



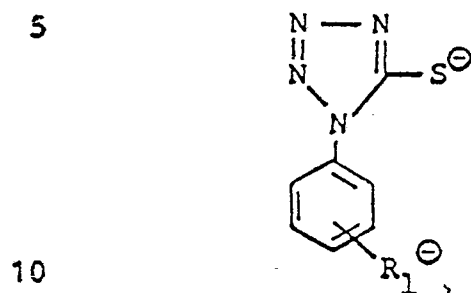
where R' is R minus a proton. The rate of release of the
 substituted phenylmercaptoazole moiety is temperature
 dependent, that is, more is released as the temperature at
 20 which processing of the film unit is effected rises. Thus,
 more of the substituted phenylmercaptoazole moiety is
 made available at elevated temperatures, i.e., above room
 temperature, where more is typically desired, less is
 released at room temperature and even less below room
 25 temperature where lesser amounts are needed. Thus, these
 blocked compounds which are utilized according to the
 invention provide more uniform sensitometry for the film
 units of the invention over a wide temperature range of
 processing. In other words, the sensitometry of the film
 30 units which include such blocked compounds according to
 the invention is less temperature dependent than would
 otherwise be the case.

The compounds which are useful according to the invention
 35 have been found to modify and/or control the sensitometry

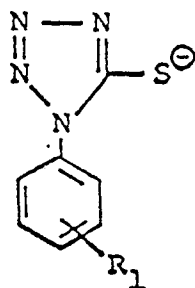
1 when present during diffusion transfer processing of an
exposed photosensitive element, particularly when such
processing is carried out at elevated temperatures, e.g.,
at about 35°C. Such modification and/or control include a
speed increase for one or more of the silver halide
5 emulsions in a multicolour diffusion transfer photographic
system and/or an increase in the D_{\max} of one or more of the
individual colours due to control of fog development, as
will be illustrated in detail below herein. The advantage-
ous results obtained through the use of the mercaptoazole
10 compounds according to the invention are not completely
understood. However, to further aid those skilled in the
art to understand and practice the invention, the proposed
theoretical mechanism by which the advantageous results
are thought to be effected will be discussed here. It
15 should be understood, however, that the diffusion transfer
photographic system has been proved to be operative and
highly effective through extensive experimentation and the
proposed theoretical mechanism is not to be construed as
being limiting of the invention. It is theorized that the
20 results obtained according to the invention are due to the
compounds performing different functions at different
stages of the development process, that is, as weak silver
solvents and promoters of development at one stage of the
development process and as development inhibitors, or
25 restrainers, at another stage of the development process,
and that the dual functions of these compounds within the
diffusion transfer photographic system are pH dependent.

It is well known that in the diffusion transfer photo-
30 graphic development process the pH of any particular
location within the film unit varies with time. Typically,
the processing composition employed in the process has a
very high pH, e.g., from about 13-14, and during the
development process each layer of the multilayer film unit
35 goes through a broad pH range which includes very high pH

1 levels and relatively low pH levels. When the pH is sub-
stantially equal to or above the pKa of the substituent R₁
on the phenyl ring, the dianion is formed, for example,



and acts as a weak silver solvent to form relatively soluble
silver salts, thus promoting development. When the pH falls
15 below the pKa of the substituent R₁, the monoanion is
formed, for example,



and the silver salt of the monoanion of the compound is
very low in solubility resulting in a development
restrainer action.

30 In the instances where certain substituted phenylmercapto-
tetrazole compounds were taught for use in specified
photographic applications, i.e., the Research Disclosure
article and U.S. Patent 3,295,976, previously cited, the
35 processes do not involve different pH at different stages

1 of the development process. Thus, the pH-dependent dual
functions of these compounds were not known or utilized in
the processes disclosed in these references.

The compounds used according to the invention may be in-
5 corporated in various locations within the diffusion trans-
fer film unit such as, for example, in the processing
composition, in one or more layers within the photosensit-
ive element or in one or more layers in the image-receiving
element such as the image-receiving layer. In view of the
10 foregoing discussion, it will be understood that, according
to the invention, development of the exposed photosensitive
element is carried out with a processing composition having
an initial pH substantially equal to or above the pKa of
 R_1 , at least for some period of time after the processing
15 composition comes into contact with the mercaptoazole
compound so as to enable the substituent to ionize to form
the dianion. In addition, at some point during the develop-
ment process the pH of the environment where the compound
is located is reduced below the pKa of R_1 so as to form the
20 monoanion.

BRIEF DESCRIPTION OF THE DRAWINGS

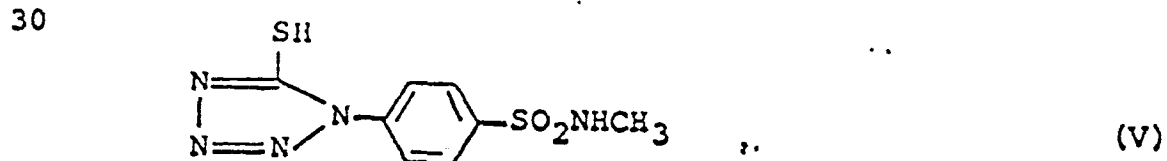
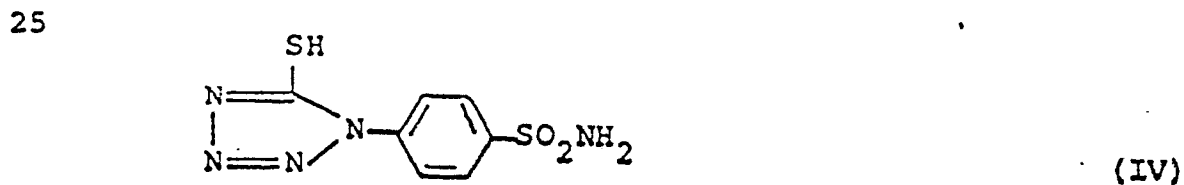
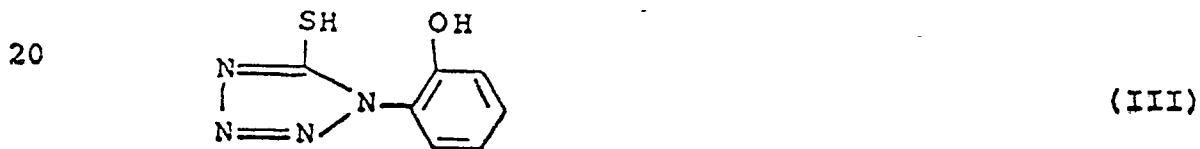
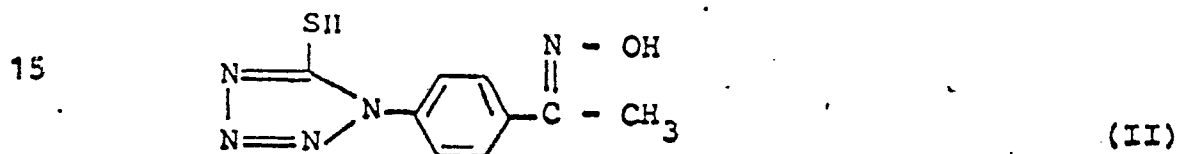
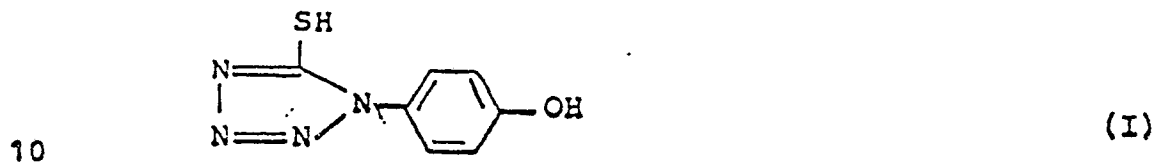
For a better understanding of the invention as well as
25 other objects and further features thereof, reference is
made to the following detailed description of various pre-
ferred embodiments thereof taken in conjunction with the
accompanying drawings wherein:

30 Fig. 1 is a graphical illustration of the relative amount
of silver developed with respect to time in exposed and
unexposed areas for a control film unit and a film unit
according to the invention, both processed at room
temperature; and

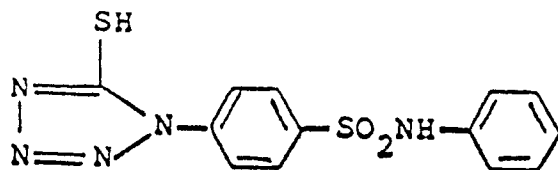
1 Fig. 2 is a similar graphical illustration for the same film units processed at 35°C.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

5 The preferred compounds which are employed in accordance with the invention are represented by the formulas

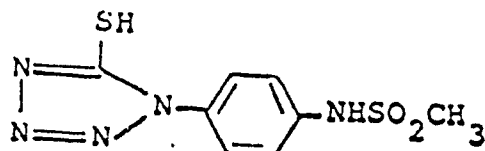


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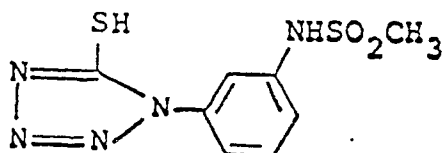
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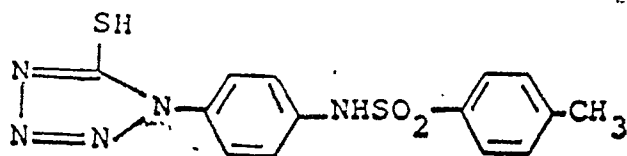
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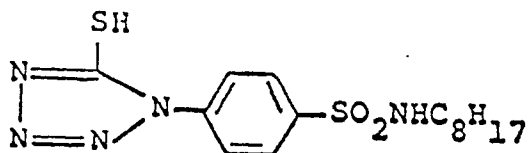
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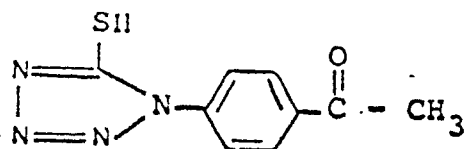
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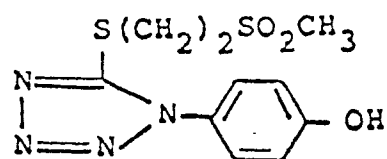
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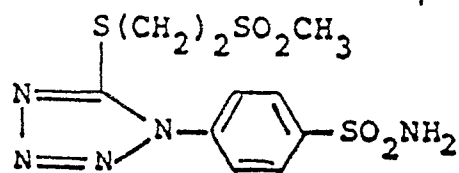
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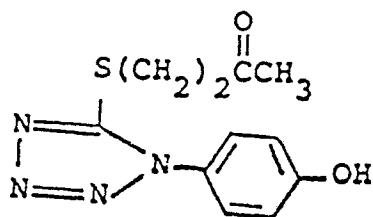
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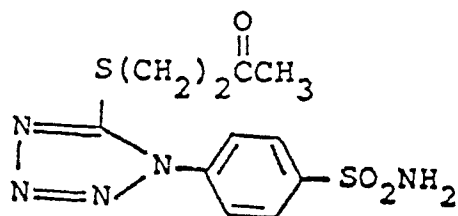
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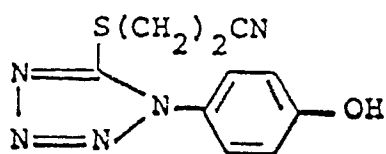
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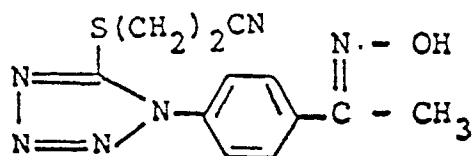
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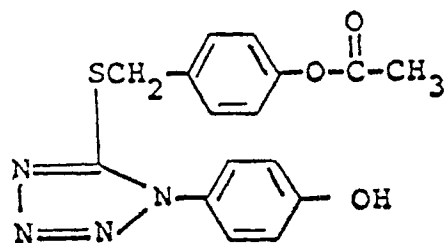
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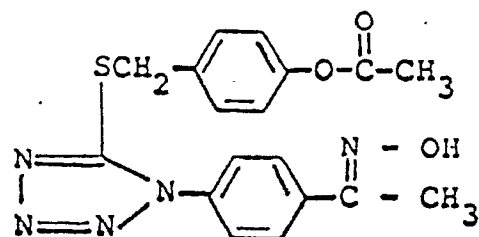
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(XVIII)

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(XIX)

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1 The mercaptoazole compounds which are useful according to
the invention may be prepared by reactions which are well
known in the art. For example, 2-mercaptoimidazoles can be
prepared by the reactions disclosed in The Chemistry of
Heterocyclic Compounds Vol. 6: Imidazole and Its Derivat-
5 ives, Part I, Hofmann, Interscience Publishers, Inc., New
York, 1953, pages 77-85; mercaptothiazoles and mercapto-
benzothiazoles can be prepared according to the methods
disclosed in The Chemistry of Heterocyclic Compounds
Vol. 34: Thiazole and Its Derivatives, Part I, Metzger,
10 John Wiley and Sons, 1979, pages 260-269; Part 2,
pages 370-377; benzoxazolethiones can be prepared according
to the methods disclosed in Heterocyclic Compounds, Vol. 5,
Elderfield, John Wiley and Sons, 1957, pages 439-444;
5-mercapto-1,3,4-oxadiazoles can be prepared according to
15 the methods disclosed in Heterocyclic Compounds, Vol. 7,
Elderfield, John Wiley and Sons, 1961, page 352; mercapto-
1,3,4-thiadiazoles, *ibid*, pages 587-612; and tetrazoles by
the techniques disclosed in Heterocyclic Compounds, Vol. 8,
Elderfield, John Wiley and Sons, 1967, pages 1-107. Mer-
20 capto-1,2,4-triazoles can be prepared by known literature
techniques as described, for example, in Jour. Chem. Soc.
E. Haggarth 1163 (1949). The compounds within Formulas A,
B and C where R is a blocking group can be prepared also
by known reactions such as by preforming the monosodium
25 salt of the appropriate mercaptoazole derivative and
carrying out a condensation reaction with the appropriate
blocking group in a solvent such as acetone, ethanol,
acetonitrile, etc., or by reacting the mercaptoazole
derivative with the appropriate blocking group in a
30 suitable solvent in the presence of one equivalent of
sodium bicarbonate. Alternatively, the appropriate mer-
captoazole derivative can be formed and the blocking group
attached by means of a Michael addition with an appropriate
olefin such as $\text{CH}_2=\text{CH}-\text{Y}$ where Y is an electron withdrawing
35 group such as cyano, etc., according to known teachings in
the art.

1 The preparation of compound I is described in Pharmazie,
29(2), (1974), pp 95-99. The preparation of compound IV
is described in Khim. Geterotsikl. Soedin., Sb.1:
Azotsoderzhashchie Geterotsikl, 1967, pp 199-201. Compounds
VI and VII can be prepared in accordance with the dis-
5 closure of U.S. Patent 3,295,976.

Compound II and Compounds XII - XIX are per se novel
compounds.

10 As stated previously, R_1 may also be a precursor of a sub-
stituent which has the requisite properties and the desired
substituent may be formed in situ. For example, where it is
desired to develop the exposed photosensitive element in
the presence of a compound within Formula A which has a
15 hydroxy group on the phenyl ring, it is possible to in-
corporate in the film unit as a precursor a compound within
Formula A which has a hydrolyzable ester group on the phenyl
ring and generate the desired hydroxy group in situ during
photographic processing.

20 It should be noted here that the acetyl group which is sub-
stituted on the phenyl ring in compound XI does not ionize
to any appreciable extent to form an anion in an aqueous
alkaline photographic processing composition. However, it
25 has been shown by experimentation that incorporating
compound XI in a film unit according to the invention will
provide advantageous results. Thus, it would appear that
compound XI undergoes a change in aqueous alkaline pro-
cessing composition and that the acetyl substituent is a
30 precursor of a group which has the requisite properties
described above which provide the desired results. It has
also been found that when incorporated in the processing
composition for a period of time, for example, about a
week or more, prior to processing of the exposed photo-
35 sensitive element, the compound does not provide the

1 the desired results, thus indicating that it has long term
 instability characteristics in the aqueous alkaline pro-
 cessing composition. It is therefore preferred to in-
 5 corporate the compound elsewhere in the film unit, for
 example, in the photosensitive element.

5

Table I lists the pKa of various substituents in certain of
 the compounds illustrated above.

10

TABLE I

<u>COMPOUND</u>	<u>pKa</u>
I	10.10 [±] 0.1
II	11.4
15 III	9.50 [±] 0.1
IV	9.95 [±] 0.1
V	11.55 [±] 0.1
VI	9.55 [±] 0.1
VII	8.65 [±] 0.1
20 IX	8.80 [±] 0.1

Solubility product measurements were made for the silver
 salt of phenylmercaptotetrazole (PMT) at pH 13.5 and for
 the silver salt of compound II at pH 7 and pH 13.5 (above
 25 and below the pKa of the oxime substituent). The results
 are listed in Table II.

TABLE II

<u>COMPOUND</u>	<u>pH</u>	<u>Ksp</u>
30 PMT	7	3 x 10 ^{-16*}
	13.5	4 x 10 ⁻¹⁶
II	7	~ 1 x 10 ⁻¹⁶
	13.5	2 x 10 ⁻¹⁵

35

* Z.C.H. Tan, Photogr.Sci.Eng. 19, 17 (1975)

- 1 It is seen that while phenylmercaptotetrazole was relative-
ly unaffected by pH the ionization of the oxime substituent
increased the solubility of the silver salt of compound II
by an order of magnitude.
- 5 The solubilities of the silver salts of PMT and compound II
in the presence of excess amounts of their anions were
measured at pH 7.0 and 13.5. Each solution was 4×10^{-3}
molar in silver. The results are shown in Table III wherein
the solubility data is expressed in $\mu\text{moles/liter}$ of total
10 silver.

TABLE III

15	Molar Ratio Compound/Ag	COMPOUND II		PMT	
		pH		pH	
		7.0	13.5	7.0	13.5
	1.25/1	<1	19	<1	1
	1.75/1	<1	44	<1	2
20	2.13/1	<1	93	1	4
	2.5/1	2	140	3	8
	4.5/1	2	320	15	18
	7.5/1	5	1400	58	63

25

It can be seen that compound II is a weak to moderate
silver solvent at high pH while PMT is not. Further, it is
evident that when the oxime substituent is protonated it
30 reverts to behaviour which is similar to that of PMT. In
fact, compound II forms an even less soluble salt in
neutral solution than does PMT, thus giving it greater
differentiation on the availability of silver in soluble
form as the pH drops in the diffusion transfer development
35 process.

1 As stated previously, the compounds which are employed
according to the invention may be incorporated in any
location in the film unit with the preferred location in
any particular instance being dependent upon various
factors such as the compound itself, the type of film unit
5 and the results desired. The compounds generally may be
incorporated in the film unit in any useful amount. Routine
scoping tests may be used to ascertain the concentration
appropriate for any given film unit and location. When the
compounds are incorporated in the processing composition
10 they are present preferably in an amount of from about
0.02 to about 0.07 % by weight. When incorporated in a
layer in the photosensitive element the compounds are
typically present in a ratio of from about 1 mg/m² to about
3 mg/m² to about 3800 mg/m² of silver. It has been observed
15 that, typically, where the compounds are incorporated in the
photosensitive element, the total amount required per film
unit to give a desired result is less than that required
when the compound is incorporated in the processing com-
position. It has also been observed that too great an amount
20 of the compounds can lead to reduced control of one or more
of the image dye-providing materials which results in high
D_{min} values in the photographic reproduction or can lead to
a loss in D_{max} for one or more colours as will be apparent
from the Examples.

25

In a preferred embodiment of the invention compounds
according to the invention can be incorporated in more than
one location in the diffusion transfer film unit. For
example, part of the total quantity of the substituted
30 phenylmercaptoazole compound can be incorporated in the
processing composition and the remainder in the photo-
sensitive element. Thus, during the initial stages of
development, the quantity available can be appropriate to
provide a speed increase for one or more silver halide
35 emulsions (silver solvent effect) without providing any

1 undesired premature development restraint and the additional
quantity dissolved during processing could give a total con-
centration desired to prevent further development. This
embodiment is particularly useful where R is H or an alkali
metal for the compound incorporated in the processing
5 composition and R is a cleavable group for the compound
incorporated in the photosensitive element.

The compounds used in accordance with the invention may be
used generally in association with any silver halide emuls-
10 ion. It is preferred to use the compounds in a diffusion
transfer photographic system which includes a negative
silver halide emulsion, i.e., one which develops in the
areas of exposure. The diffusion transfer photographic
system of the invention may include any image dye-providing
15 material in association with the silver halide emulsion(s).

The image dye-providing materials which can be utilized
generally may be characterized as either (1) initially
soluble or diffusible in the processing composition but
20 which are selectively rendered nondiffusible imagewise as
a function of development; or (2) initially insoluble or
nondiffusible in the processing composition but which
selectively provide a diffusible product imagewise as a
function of development. The image dye-providing materials
25 may be complete dyes or dye intermediates, e.g., colour
couplers. The requisite differential in mobility or
solubility may be obtained, for example, by a chemical
reaction such as a redox reaction, a coupling reaction or
a cleavage reaction. In a particularly preferred embodiment
30 of the invention the image dye-providing materials are dye
developers which are initially diffusible materials. The
dye developers contain, in the same molecule, both the
chromophoric system of a dye and a silver halide developing
function as is described in U.S. Patent 2,983,606. Other
35 image dye-providing materials which may be used include,

1 for example, initially diffusible coupling dyes such as
are useful in the diffusion transfer process described in
U.S. Patent 3,087,817 and which are rendered nondiffusible
by coupling with the oxidation product of a colour
developer; initially nondiffusible dyes which release a
5 diffusible dye following oxidation, sometimes referred to
as "redox dye releaser" dyes, such as described in U.S.
Patents 3,725,062 and 4,076,529; initially nondiffusible
image dye-providing materials which release a diffusible
dye following oxidation and intramolecular ring closure
10 as are described in U.S. Patent 3,433,939 or undergo silver
assisted cleavage to release a diffusible dye in accordance
with the disclosure of U.S. Patent 3,719,489; and initially
nondiffusible image dye-providing materials which release a
diffusible dye following coupling with an oxidized colour
15 developer as described in U.S. Patent 3,227,550.

The compounds may be incorporated into the photographic
elements by any suitable technique. In embodiments where
the compounds are incorporated in a separate discrete
20 layer or in a silver halide emulsion layer they are
typically coated from a water dispersion and the layer
includes a binder material such as gelatin or the like.

The diffusion transfer film units of the invention include
25 those wherein the image receiving element is designed to be
separated from the photosensitive element after processing
and integral positive-negative diffusion transfer film
units which are retained intact after processing. In a
preferred embodiment the diffusion transfer film units of
30 the invention utilize initially diffusible dye developers
as the image dye-providing materials. As described in U.S.
Patent 2,983,606, a photosensitive element containing a
dye developer and a silver halide emulsion is photoexposed
and a processing composition applied thereto, for example,
35 by immersion, coating, spraying, flowing, etc., in the

1 dark. The exposed photosensitive element is superposed
prior to, during, or after the processing composition is
applied, on a sheet-like support element which may be
utilized as an image-receiving element. In a preferred
embodiment, the processing composition is applied to the
5 exposed photosensitive element in a substantially uniform
layer as the photosensitive element is brought into super-
posed relationship with the image-receiving layer. The
processing composition, positioned intermediate the photo-
sensitive element and the image-receiving layer, permeates
10 the emulsion to initiate development of the latent image
contained therein. The dye developer is immobilized or
precipitated in exposed areas as a consequence of the
development of the latent image. This immobilization is
apparently, at least in part, due to a change in the
15 solubility characteristics of the dye developer upon
oxidation and especially as regards its solubility in
alkaline solutions. It may also be due in part to a tanning
effect on the emulsion by oxidized developing agent, and in
part to a localized exhaustion of alkali as a result of
20 development. In unexposed and partially exposed areas of
the emulsion, the dye developer is unreacted and diffusible
and thus provides an imagewise distribution of unoxidized
dye developer, diffusible in the processing composition,
as a function of the point-to-point degree of exposure of
25 the silver halide emulsion. At least part of this imagewise
distribution of unoxidized dye developer is transferred, by
imbibition, to a superposed image-receiving layer or
element, said transfer substantially excluding oxidized dye
developer. The image-receiving layer receives a depthwise
30 diffusion, from the developed emulsion, of unoxidized dye
developer without appreciably disturbing the imagewise
distribution thereof to provide a reversed or positive
colour image of the developed image. The image-receiving
element may contain agents adapted to mordant or otherwise
35 fix the diffused, unoxidized dye developer. In a preferred

1 In a preferred embodiment of said U.S. Patent No.
2,983,606 and in certain commercial applications thereof,
the desired positive image is revealed by separating the
image-receiving layer from the photosensitive element at
the end of a suitable imbibition period. Alternatively, as
5 also disclosed in said U.S. Patent No. 2,983,606, the
image-receiving layer need not be separated from its super-
posed contact with the photosensitive element, subsequent
to transfer image formation, if the support for the image-
receiving layer, as well as any other layers intermediate
10 said support and image-receiving layer, is transparent and
a processing composition containing a substance, e.g., a
white pigment, effective to mask the developed silver halide
emulsion or emulsions is applied between the image-receiving
layer and said silver halide emulsion or emulsions.

15 Dye developers, as noted in said U.S. Patent No. 2,983,606,
are compounds which contain, in the same molecule, both the
chromophoric system of a dye and also a silver halide
developing function. By "a silver halide developing function"
20 is meant a grouping adapted to develop exposed silver
halide. A preferred silver halide development function is
a hydroquinonyl group. In general, the development function
includes a benzenoid developing function, that is, an
aromatic developing group which forms quinonoid or quinone
25 substances when oxidized.

Multicolour images may be obtained using dye developers in
diffusion transfer processes by several techniques. One
such technique contemplates obtaining multicolour transfer
30 images utilizing dye developers by employment of an
integral multilayer photosensitive element, such as is
disclosed in the aforementioned U.S. Patent No. 2,983,606
and in U.S. Patent No. 3,345,163, wherein at least two
selectively sensitized photosensitive strata, superposed on
35 a single support, are processed, simultaneously and without

1 separation, with a single common image-receiving layer. A
suitable arrangement of this type comprises a support carry-
ing a red-sensitive silver halide emulsion stratum, a
green-sensitive silver halide emulsion stratum and a blue-
sensitive silver halide emulsion stratum, said emulsions
5 having associated therewith, respectively, for example, a
cyan dye developer, a magenta dye developer and a yellow
dye developer. The dye developer may be utilized in the
silver halide emulsion stratum, for example in the form of
10 particles, or it may be disposed in a stratum behind the
appropriate silver halide emulsion strata. Each set of
silver halide emulsion and associated dye developer strata
may be separated from other sets by suitable interlayers,
for example, by a layer or stratum of gelatin or polyvinyl
alcohol. In certain instances, it may be desirable to in-
15 corporate a yellow filter in front of the green-sensitive
emulsion and such yellow filter may be incorporated in an
interlayer. However, where desirable, a yellow dye
developer of the appropriate spectral characteristics and
present in a state capable of functioning as a yellow
20 filter may be so employed and a separate yellow filter
omitted.

Particularly useful products for obtaining multicolour dye
developer images are disclosed in U.S. Patent No. 3,415,644.
25 This patent discloses photographic products wherein a
photosensitive element and an image-receiving element are
maintained in fixed relationship prior to exposure, and
this relationship is maintained as a laminate after pro-
cessing and image formation. In these products, the final
30 image is viewed through a transparent (support) element
against a light-reflecting, i.e., white background. Photo-
exposure is made through said transparent element and
application of the processing composition provides a layer
of light-reflecting material to provide a white background.
35 The light-reflecting material (referred to in said patent

1 as an "opacifying agent") is preferably titanium dioxide,
and it also performs an opacifying function, i.e. it is
effective to mask the developed silver halide emulsions
so that the transfer image may be viewed without inter-
ference therefrom, and it also acts to protect the photo-
5 exposed silver halide emulsions from postexposure fogging
by light passing through said transparent layer if the
photoexposed film unit is removed from the camera before
image-formation is completed.

10 U.S. Patent No. 3,647,437 is concerned with improvements
in products and processes disclosed in said U.S. Patent
No. 3,415,644, and discloses the provision of light-absorb-
ing materials to permit such processes to be performed,
outside of the camera in which photoexposure is effected,
15 under much more intense ambient light conditions. A light-
absorbing material or reagent, preferably a pH-sensitive
phthalein dye, is provided so positioned and/or constituted
as not to interfere with photoexposure but so positioned
between the photoexposed silver halide emulsions and the
20 transparent support during processing after photoexposure
as to absorb light which otherwise might fog the photo-
exposed emulsions. Furthermore, the light-absorbing
material is so positioned and/or constituted after pro-
cessing as not to interfere with viewing the desired image
25 shortly after said image has been formed. In the preferred
embodiments, the light-absorbing material, also sometimes
referred to as an optical filter agent, is initially con-
tained in the processing composition together with a
light-reflecting material, e.g., titanium dioxide. The
30 concentration of the light-absorbing dye is selected to
provide the light transmission opacity required to perform
the particular process under the selected light conditions.

In a particularly useful embodiment, the light-absorbing
35 dye is highly coloured at the pH of the processing

1 composition, e.g., 13-14, but is substantially non-absorb-
ing of visible light at a lower pH, e.g., less than 10-12.
This pH reduction may be effected by an acid-reacting
reagent appropriately positioned in the film unit, e.g., in
a layer between the transparent support and the image-
5 receiving layer.

The dye developers are preferably selected for their
ability to provide colors that are useful in carrying out
subtractive colour photography, that is, the previously
10 mentioned cyan, magenta and yellow. The dye developers
employed may be incorporated in the respective silver
halide emulsion or, in the preferred embodiment, in a
separate layer behind the respective silver halide
emulsion, and such a layer of dye developer may be applied
15 by use of a coating solution containing the respective dye
developer distributed, in a concentration calculated to
give the desired coverage of dye developer per unit area,
in a film-forming natural, or synthetic, polymer, for
example, gelatin, polyvinyl alcohol, and the like, adapted
20 to be permeated by the processing composition.

Other diffusion transfer products and processes according
to the invention are the types described in U.S. Patents
3,573,043 and 3,594,165. For convenience, the entire dis-
25 closure of each of the six patents referred to immediately
above is hereby incorporated by reference herein.

A particularly useful film unit according to the invention
is one wherein the photosensitive element includes a
30 light-reflecting layer between the silver halide layer and
the image dye-providing layer (as described in Canadian
Patent 668,952), the substrate of the photosensitive
element carries the polymeric acid neutralizing layer
which in turn carries the timing layer (as described in
35 U.S. Patent 3,573,043) and the processing composition

1 includes an oximated polydiacetone acrylamide thickening agent (as described in U.S. Patent 4,202,694).

The invention will now be described further in detail with respect to specific preferred embodiments by way of
 5 examples, it being understood that these are illustrative only and the invention is not intended to be limited to the materials, conditions, process parameters, etc. which are recited therein. All parts and percentages are by weight unless otherwise indicated.

10

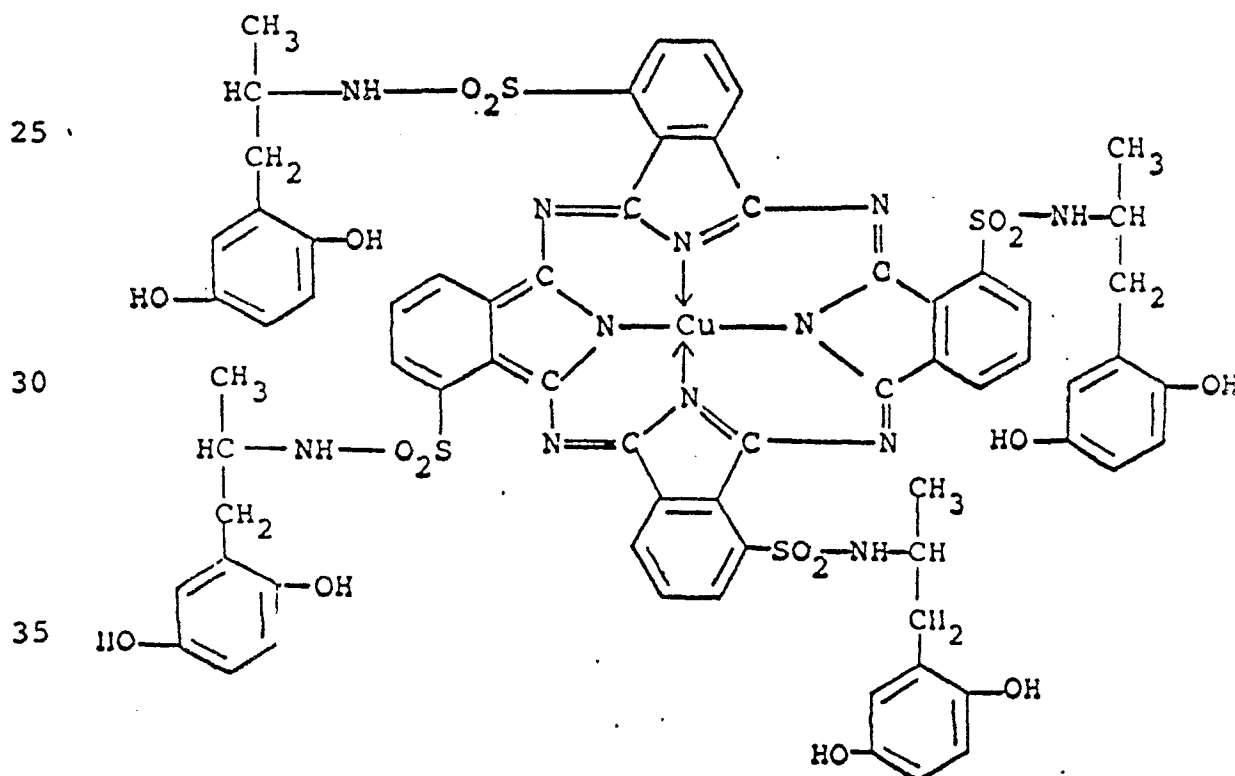
EXAMPLE I

As a control a film unit was prepared as follows: The photosensitive element comprised a subcoated transparent
 15 polyethylene terephthalate photographic film base having coated thereon the following layers in succession:

1. a layer of sodium cellulose sulfate coated at a coverage of about 27.6 mg/m²;

20

2. a layer of a cyan dye developer represented by the formula



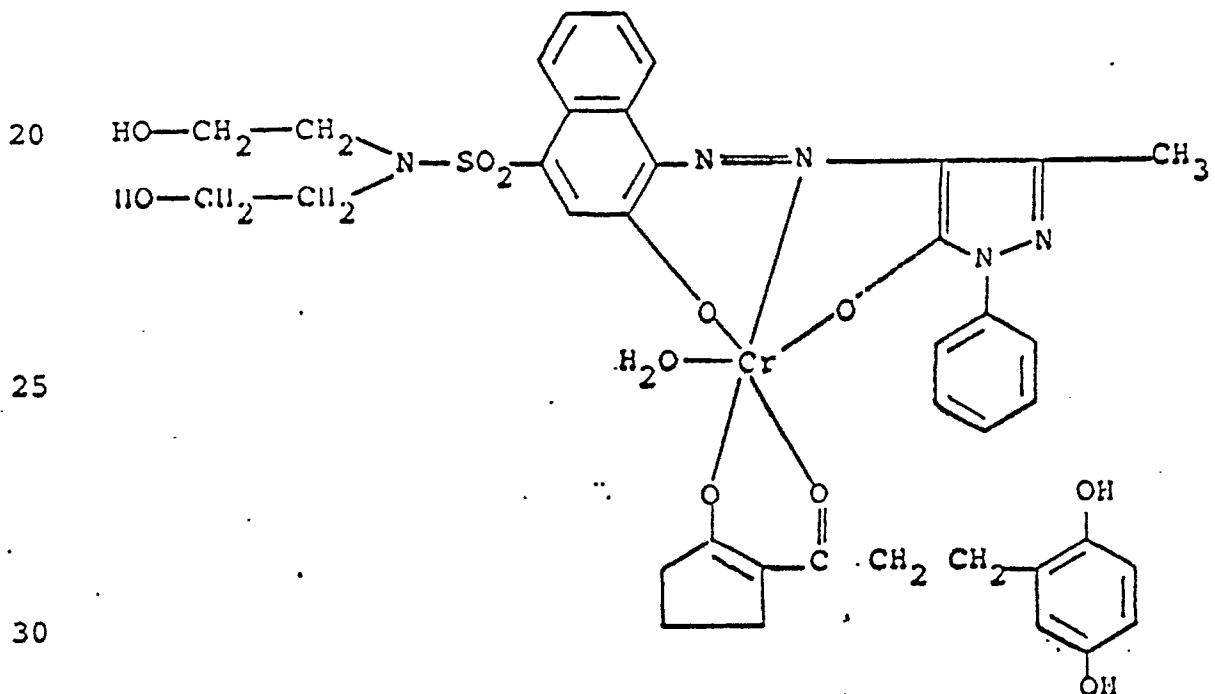
- 28 -

1 dispersed in gelatin and coated at a coverage of about
747 mg/m² of the dye developer and about 1554 mg/m² of
gelatin and including about 68 mg/m² of 4'-methylphenyl-
hydroquinone and about 270 mg/m² of 2-phenylbenzimidazole;

5 3. a red-sensitive silver iodobromide emulsion layer
coated at a coverage of about 1280 mg/m² of silver and
about 768 mg/m² of gelatin;

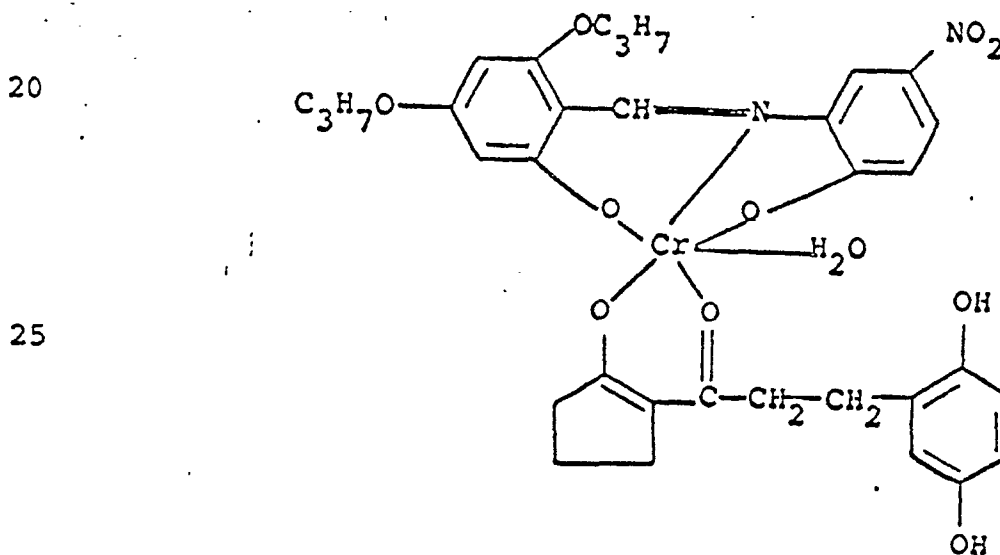
4. an interlayer comprising about 2505 mg/m² of a
10 60-29-6-4-0.4 pentapolymer of butylacrylate, diacetone
acrylamide, methacrylic acid, styrene and acrylic acid
and about 78 mg/m² of polyacrylamide;

5. a layer of a magenta dye developer represented by the
15 formula



35

- 1 dispersed in gelatin and coated at a coverage of about
646 mg/m² of the dye developer, about 448 mg/m² of gelatin
and including about 229 mg/m² of 2-phenylbenzimidazole;
6. a green-sensitive silver iodobromide layer coated at
5 a coverage of about 1050 mg/m² of silver and about 504 mg/m²
of gelatin;
7. a layer comprising about 215 mg/m² of dodecyl-amino-
reductone and about 215 mg/m² of gelatin;
- 10 8. an interlayer comprising about 1366 mg/m² of the
pentapolymer described in layer 4, about 87 mg/m², about
78 mg/m² of polyacrylamide and about 71 mg/m² of succindi-
aldehyde;
- 15 9. a layer of a yellow dye developer represented by the
formula



- 30 dispersed in gelatin and coated at a coverage of about
968 mg/m² of dye developer and about 451 mg/m² of gelatin
and including about 208 mg/m² of phenylbenzimidazole;
- 35 10. a blue-sensitive silver iodobromide emulsion layer

- 30 -

1 coated at a coverage of about 1280 mg/m² of silver, about
775 mg/m² of gelatin and about 306 mg/m² of 4-methyl phenyl
hydroquinone;

11. an overcoat layer coated at a coverage of about
5 461 mg/m² of gelatin and about 21 mg/m² of carbon black.

The image-receiving element comprised a transparent poly-
ethylene terephthalate film base coated with the following
layers in succession:

10

1. as a polymeric acid layer approximately 9 parts of a
1/2 butyl ester of polyethylene/maleic anhydride copolymer
and 1 part of polyvinyl butyral coated at a coverage of
about 26,372 mg/m²;

15

2. a timing layer containing about 4575 mg/m² of a 60-30-
4-6 tetrapolymer of butylacrylate, diacetone acrylamide,
styrene and methacrylic acid and including 9 % polyvinyl
alcohol; and

20

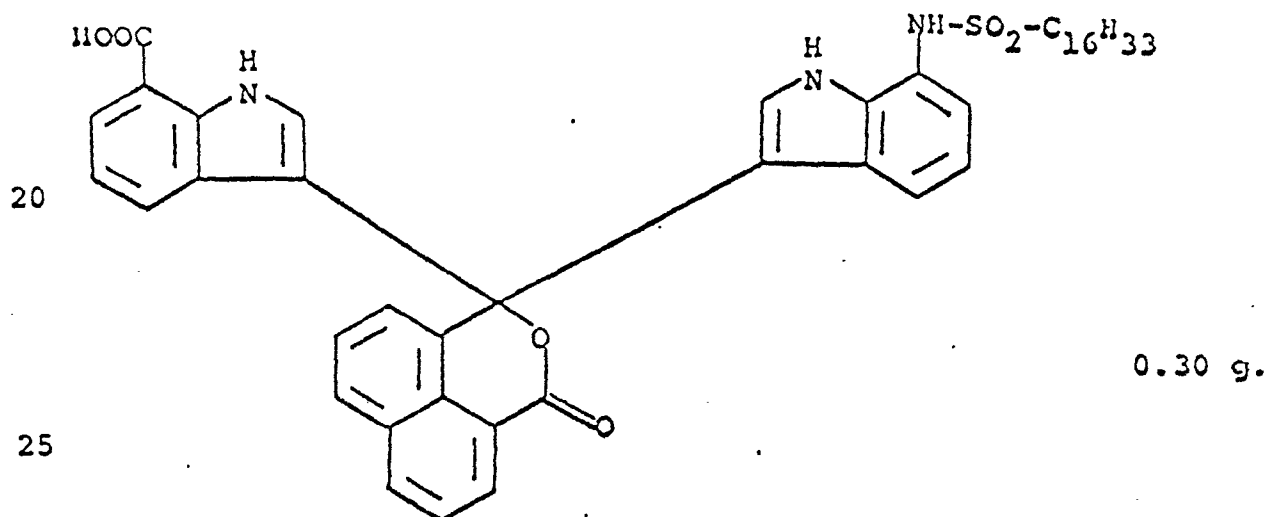
3. a polymeric image receiving layer of: (a) 3 parts of a
mixture of 2 parts polyvinyl alcohol and 1 part poly-4-
vinyl pyridine and (b) 1 part of a graft copolymer
comprised of 4-vinylpyridine (4VP) and vinylbenzyl tri-
25 methyl ammonium chloride (TMQ) grafted onto hydroxyethyl
cellulose (HEC) at a ratio of HEC/4VP/TMQ of 2.2/2.2/1
coated at a coverage of about 3229 mg/m².

30

The film unit was processed with an aqueous alkaline
processing composition as follows:

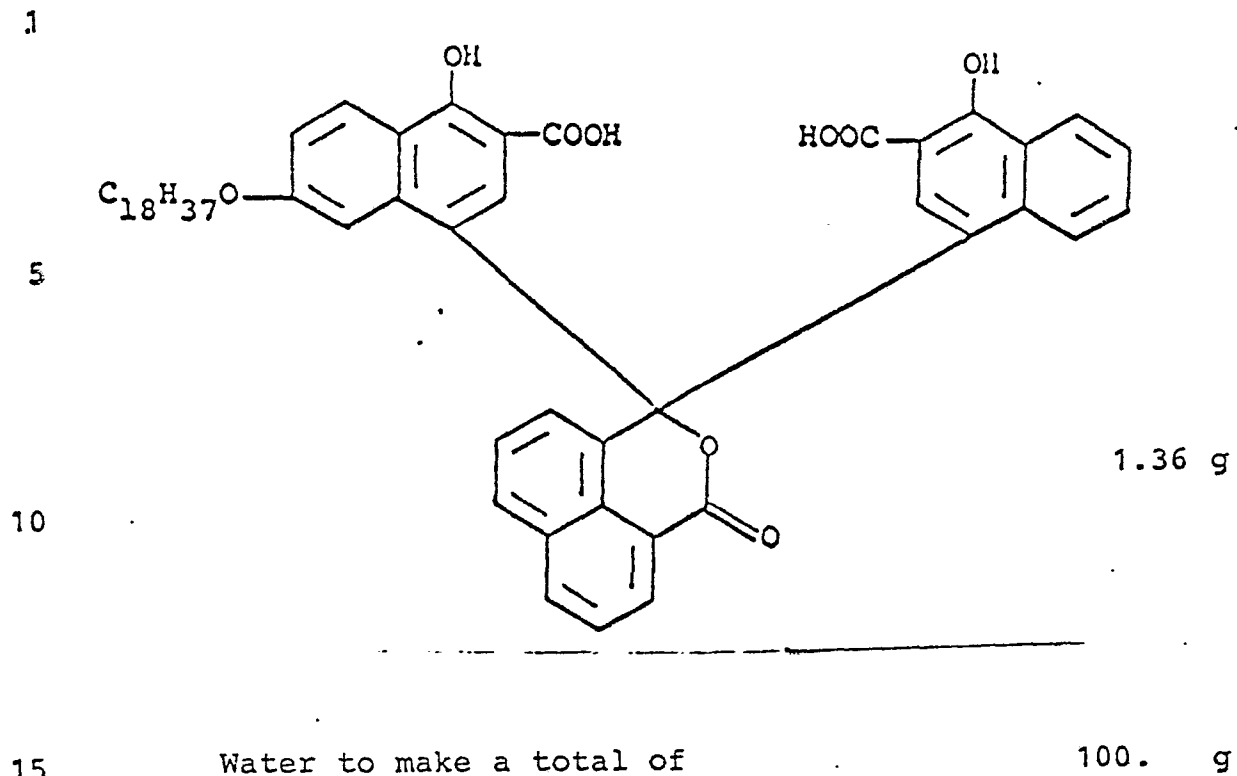
35

1	Titanium dioxide	38.05 g.
	Carboxymethyl hydroxyethyl cellulose	2.00 g.
	Potassium hydroxide (45% aqueous solution)	11.11 g.
	Benzotriazole	0.28 g.
5	6-methyl uracil	0.30 g.
	N-hydroxyethyl-N,N',N'-tris-carboxymethyl ethylene diamine	0.75 g.
	Polyethylene glycol (MW 4000)	0.45 g.
10	Bis(2-aminoethyl)sulfide	0.02 g.
	Colloidal silica (30% aqueous dispersion)	1.85 g.
	N-phenethyl- α -picolinium bromide (50% aqueous solution)	2.55 g.
15	4-aminopyrazolo(3,4-d)pyrimidine	0.25 g.



30

35



A film unit according to the invention was prepared identical to the control with the exception that the processing composition further included 0.05 % of compound II.

20 The film units were processed at room temperature as follows: one half of each film unit was exposed through the transparent base of the image-receiving element to light from a Xenon source (100 meter candle seconds) which was

25 passed in turn through an ultraviolet filter, neutral density filters to reduce the film plane light flux to 0.5 m c s, and a Wratten 47B blue filter; the other half of each film unit was not exposed. The film units were then processed by passing them through a pair of rollers at a

30 gap spacing of about 0.08 mm and the relative amount of silver developed (a function of the infra-red light absorbed) was measured as a function of time for both the exposed and unexposed areas. The relative amount of developed silver vs time curves are shown in Fig. 1. It

35 is seen that the presence of compound II reduced fog.

1 development (relative amount of developed silver in un-
exposed areas) in comparison to the control. It is also
apparent that the difference between the relative amount
of silver developed in exposed and unexposed regions in
the presence of compound II is significantly greater than
5 the corresponding difference for the control.

The experiment was repeated with processing being carried
out at 35°C. The relative amounts of developed silver vs
time curves are shown in Fig. 2. It is seen that fog
10 development in the control increased significantly at the
higher processing temperature, whereas the increase was
only slight with compound II present. Further, at the
higher processing temperature the presence of compound II
greatly reduced fog development in comparison to the
15 control without any appreciable change in the rate at
which exposed silver halide was developed.

EXAMPLE II

20 As a control a film unit was prepared as follows: The
photosensitive element comprised a subcoated opaque poly-
ethylene terephthalate photographic film base having
coated thereon the following layers in succession:

25 1. a cyan dye developer layer coated at a coverage of
about 742 mg/m² of the cyan dye developer described in
Example I, about 1485 mg/m² of gelatin, about 68 mg/m² of
4'-methylphenylhydroquinone and about 270 mg/m² of
2-phenylbenzimidazole;

30 2. a red-sensitive silver iodobromide emulsion layer
coated at a coverage of about 1290 mg/m² of silver and
about 775 mg/m² of gelatin;

35 3. an interlayer of a 60-30-4-6 tetrapolymer of butyl

- 1 acrylate, diacetone acrylamide, styrene and methacrylic
acid coated at a coverage of about 2582 mg/m² of the tetra-
polymer and about 68 mg/m² of polyacrylamide;
4. a magenta dye developer layer coated at a coverage of
5 about 646 mg/m² of the magenta dye developer described in
Example I, about 452 mg/m² of gelatin, about 11 mg/m² of
carbon black and about 226 mg/m² of 2-phenylbenzimidazole;
5. a green-sensitive silver iodobromide layer coated at a
10 coverage of about 795 mg/m² of silver and about 525 mg/m²
of gelatin;
6. an interlayer including about 1452 mg/m² of the tetra-
polymer described in layer 3, about 75 mg/m² of polyacryl-
15 amide and about 71 mg/m² of succindialdehyde;
7. a yellow dye developer layer coated at a coverage of
about 968 mg/m² of the yellow dye developer described in
Example I, about 452 mg/m² of gelatin, about 27 mg/m² of
20 carbon black and about 204 mg/m² of 2-phenylbenzimidazole;
8. a blue-sensitive silver iodobromide emulsion layer
coated at a coverage of about 1280 mg/m² of silver, about
563 mg/m² of gelatin and about 204 mg/m² of 4'-methyl
25 phenyl hydroquinone;
9. an overcoat layer coated at a coverage of about
484 mg/m² of gelatin and about 43 mg/m² of carbon black.
- 30 The image-receiving element was identical to that described
in Example I.

The film unit was processed with a control aqueous alkaline
processing composition which was the same as the control
35 described in Example I with the exception that it included

1 0.55 g of benzotriazole and did not include any 4-amino-
pyrazolo (3,4-d)pyrimidine.

The film unit was exposed (0.5 meter-candle-seconds) on a
sensitometer to a photographic test exposure scale, or
5 step wedge, through the transparent support of the image-
receiving element and processed at 24°C with the processing
composition by passing the film unit through a pair of
pressure rollers set at a gap spacing of about 0.08 mm.
The film unit was retained intact and viewed through the
10 transparent base. There was obtained a well developed image.

The neutral density column of the image was read on the
densitometer to obtain the D_{max} values for red, green and
blue curves, respectively. In addition, the speed of the
15 red, green and blue curves, respectively (defined as the
negative log of the relative exposure required to give red,
green and blue absorption in the neutral column a reflect-
ion density of 0.75) was measured. The values obtained are
shown in Table IV.

20 The experiment was repeated with five additional film units
(IIA-IIIE) with the exception that the processing composi-
tion further included compound XI in the amounts shown in
Table IV.

25

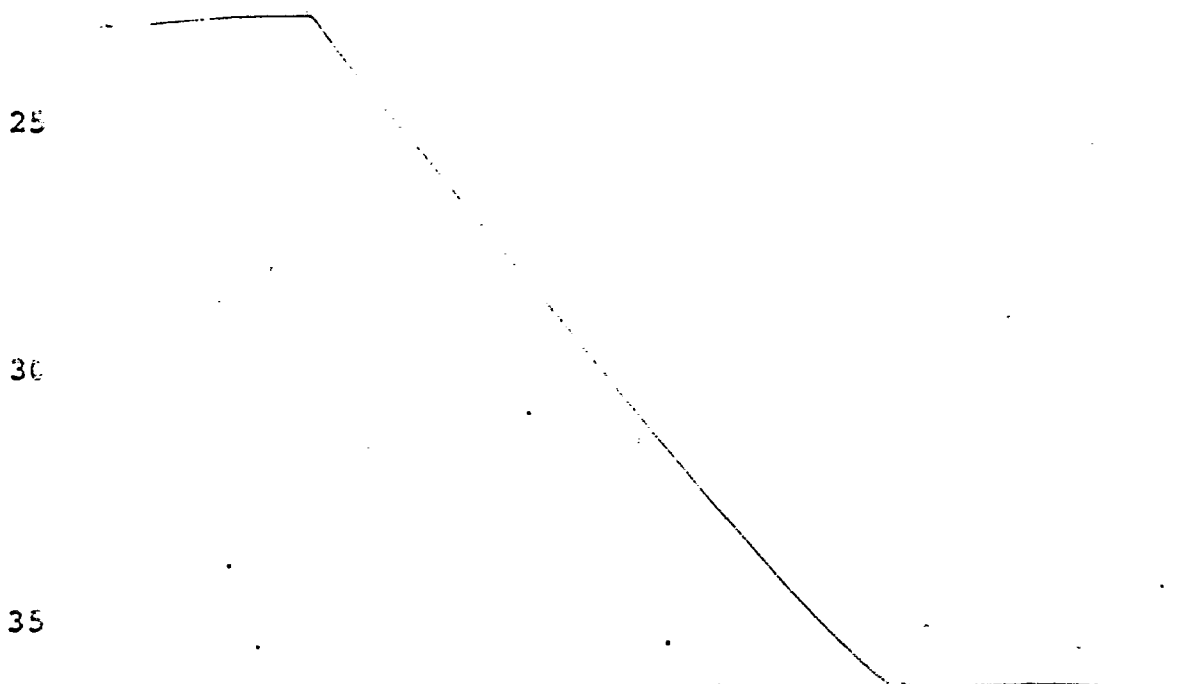
TABLE IV

Film Unit	% Comp'd XI	Dmax			Rel. Speed		
		R	G	B	R	G	B
Control	---	2.31	2.20	2.22	1.41	1.29	1.23
30 IIA	0.013	2.36	2.23	2.31	1.45	1.42	1.45
IIE	0.025	2.36	2.21	2.25	1.45	1.45	1.53
IIC	0.05	2.37	2.17	2.18	1.45	1.49	1.50
IID	0.075	2.36	2.18	2.24	1.43	1.45	1.27
35 IIE	0.1	2.34	2.16	2.23	1.40	1.33	0.44

1 It can be seen that the presence of compound XI provided
a slight increase in the D_{\max} of the individual colours at
certain concentrations and also provided an appreciable
increase in the green and blue speeds at certain concentrat-
ions. Thus it is apparent that in this case about 0.025 % of
5 compound XI gave the optimum combination of speed increase
and D_{\max} increase. The data also show that in a given film
unit excessive concentrations of the compound for that
film unit can lead to undesirable results; thus in Film
Unit IIE the blue speed dropped considerably indicating
10 premature inhibition of development of the blue-sensitive
silver halide layer.

EXAMPLE III

15 The experiment described in Example II was repeated with
six film units (IIIA-IIIF) which included compound II in
the amounts shown in Table V. In addition, certain of the
film units were also processed at 35°C. The room temperature
data for the control film unit of Example II were used for
20 comparison. In addition, a control film unit was processed
at 35°C.



- 37 -

1

TABLE V

24 °C

Film Unit	% Comp'd II	D _{max}			Rel. Speed		
		R	G	B	R	G	B
Control	---	2.31	2.20	2.22	1.41	1.29	1.23
5 IIIA	0.05	2.39	2.24	2.36	1.36	1.35	1.38
IIIB	0.06	2.43	2.28	2.38	1.39	1.40	1.44
IIIC	0.07	2.42	2.25	2.35	1.38	1.40	1.46
IIID	0.08	2.36	1.97	2.13	1.35	1.41	1.48
IIIE	0.09	2.35	1.91	2.04	1.40	1.48	1.55
10 IIIF	0.10	2.32	1.81	1.88	1.40	1.52	1.60

35 °C

Film Unit	% Comp'd II	Δ D _{max}			Δ Rel. Speed		
		R	G	B	R	G	B
Control		-0.45	-0.28	-0.45	+0.10	+0.16	+0.08
15 IIIA	0.05	-	-	-	-	-	-
IIIB	0.06	-0.20	-0.05	-0.12	+0.05	+0.01	-0.08
IIIC	0.07	-0.17	-0.02	-0.10	+0.04	+0.01	-0.08
IIID	0.08	-0.13	+0.26	+0.12	+0.07	+0.02	-0.06
IIIE	0.09	-0.07	+0.33	+0.23	+0.02	-0.04	-0.10
20 IIIF	0.10	-	-	-	-	-	-

The results show that at room temperature processing (24°C) the presence of compound II provided an increase in the D_{max} of the individual colours at concentrations up to 25 0.07 % and an increase in the green and blue speeds in each film unit. When the film units were processed at 35°C the presence of compound II provided a significant improvement over the control in D_{max} since the D_{max} of the individual colours went down considerably less, in comparison to the 30 values obtained at 24°C, in most instances, and actually increased in others.

EXAMPLE IV

Two sets of film units, identical to those described in Example II except that the processing composition of one (IVA) contained 0.025 % of compound XI and that of the other, (IVB) contained 0.05 % of compound II were processed at 24°C and 35°C. The data are shown in Table VI. The data for the control film unit of Example II were used for comparison.

TABLE VI

Film Unit	24°C					
	Dmax			Rel. Speed		
	R	G	B	R	G	B
Control	2.31	2.20	2.22	1.41	1.29	1.23
IVA	2.36	2.21	2.25	1.45	1.45	1.53
IVB	2.27	2.22	2.26	1.39	1.39	1.42
Film Unit	35°C					
	Δ Dmax			Δ Rel. Speed		
	R	G	B	R	G	B
Control	-0.45	-0.28	-0.45	+0.10	+0.16	+0.08
IVA	-0.25	+0.01	-0.01	+0.04	-0.03	-0.12
IVB	-0.15	-0.01	+0.02	+0.08	+0.05	-0.04

It can be seen that again the presence of compounds XI and II provided significant increases in the green and blue relative speeds at 24°C and provided significant improvement in the red, green and blue D_{max} at 35°C, with the relative speeds of these colours being desirably closer than in the control.

EXAMPLE V

A control film unit was prepared as follows: The photosensitive element comprised a subcoated opaque polyethylene terephthalate photographic film base having coated thereon

1 in succession:

1. a layer of sodium cellulose sulfate coated at a coverage of about 14 mg/m²;
- 5 2. a cyan dye developer layer comprising about 747 mg/m² of the cyan dye developer illustrated in Example I, about 1554 mg/m² of gelatin, about 207 mg/m² of 2-phenylbenzimidazole and about 68 mg/m² of 4'-methyl phenyl hydroquinone;
- 10 3. a red-sensitive silver iodobromide emulsion layer coated at a coverage of about 1280 mg/m² of silver and about 768 mg/m² of gelatin;
- 15 4. an interlayer comprising about 1882 mg/m² of the pentapolymer described in Example I and about 58 mg/m² of polyacrylamide;
- 20 5. a magenta dye developer layer comprising about 545 mg/m² of the magenta dye developer illustrated in Example I, about 382 mg/m² of gelatin and about 230 mg/m² of 2-phenylbenzimidazole;
- 25 6. a green-sensitive silver iodobromide emulsion layer coated at a coverage of about 560 mg/m² of silver and about 246 mg/m² of gelatin;
- 30 7. a green-sensitive silver iodobromide emulsion layer coated at a coverage of about 1050 mg/m² of silver and about 504 mg/m² of gelatin;
8. an interlayer comprising about 1598 mg/m² of the pentapolymer described in Example I, about 102 mg/m² of polyacrylamide and about 82.5 mg/m² of succindialdehyde;
- 35 9. a yellow dye developer layer comprising about 820 mg/m².

1 of the yellow dye developer illustrated in Example I, about
385 mg/m² of gelatin and about 207 mg/m² of 2-phenylbenz-
imidazole;

10. a blue-sensitive silver iodobromide emulsion layer
5 coated at a coverage of about 1280 mg/m² of silver, about
775 mg/m² of gelatin and about 306 mg/m² of 4'-methyl-
phenyl hydroquinone; and

11. a topcoat layer of about 484 mg/m² of gelatin.

10

The image-receiving element comprised a transparent sub-
coated polyethylene terephthalate film base, on which the
following layers were coated in succession:

15 1. as a polymeric acid layer approximately 9 parts of a
1/2 butyl ester of polyethylene/maleic anhydride copolymer,
and 1 part of polyvinyl butyral coated at a coverage of
about 26,372 mg/m²;

20 2. a timing layer coated at a coverage of about 10,000 mg/
m² of a graft tetrapolymer of diacetone acrylamide, acryl-
amide, β -cyanoethylacrylate and 2-acrylamido-2-methane
sulfonic acid on polyvinylalcohol;

25 3. a polymeric image receiving layer coated at a coverage
of about 2200 mg/m² of: (a) 3 parts of a mixture of 2 parts
polyvinyl alcohol and 1 part poly-4-vinylpyridine and (b)
1 part of a graft copolymer comprised of 4-vinylpyridine
(4VP) and vinyl benzyltrimethyl ammonium chloride (TMQ)
30 grafted onto hydroxyethyl cellulose (HEC) at a ratio HEC/
4VP/TMQ of 2.2/2.2/1; and about 74 mg/m² of 1,4-butanediol
diglycidyl ether;

4. a top coat layer comprising about 320 mg/m² of poly-
35 vinylalcohol.

1 The film unit was processed with the processing composition described in Example I as a control with the exception that it included 0.55 g of benzotriazole and 0.93 g of the aqueous colloidal silica dispersion.

5 Also four additional film units (VA-VD) were prepared and processed in the same manner with the exception that the processing composition further included compound I in the amounts shown in Table VII. An identical set of film units was also processed at 35°C.

10

TABLE VII

Film Unit	% Comp'd I	24°C					
		D _{max}			Rel. Speed		
		R	G	B	R	G	B
15 Control	-	1.63	1.87	2.04	1.61	1.49	1.40
VA	0.025	1.61	1.92	2.01	1.59	1.45	1.35
VB	0.05	1.58	1.95	2.15	1.57	1.45	1.37
VC	0.1	1.56	1.98	2.11	1.62	1.55	1.48
20 VD	0.2	1.40	1.82	1.89	1.64	1.58	1.43
		35°C					
		Δ D _{max}			Δ Rel. Speed		
		R	G	B	R	G	B
Control	-	-0.58	-0.41	-0.45	0.00	-0.02	-0.06
VA	0.025	-0.39	-0.33	-0.27	-0.06	-0.03	-0.05
25 VB	0.05	-0.21	-0.19	-0.19	-0.05	-0.04	-0.07
VC	0.1	-0.09	-0.21	-0.09	-0.10	-0.10	-0.03
VD	0.2	-0.02	-0.08	+0.05	-0.05	+0.06	+0.13

30 It can be seen that at room temperature processing the presence of compound I provided an increase in the green and blue D_{max} at concentrations up to 0.1 % without any appreciable loss in relative speed. At 35°C processing the presence of compound I gave a much smaller loss in D_{max}

35 for red, green and blue in comparison to the control,

1 again without any significant change in the relative
speeds.

EXAMPLE VI

5 This experiment represents a comparison of compounds I and II
and phenylmercaptotetrazole (PMT) with a control at room
temperature.

The control film unit comprised a subcoated opaque film base
10 having the following layers coated thereon in succession:

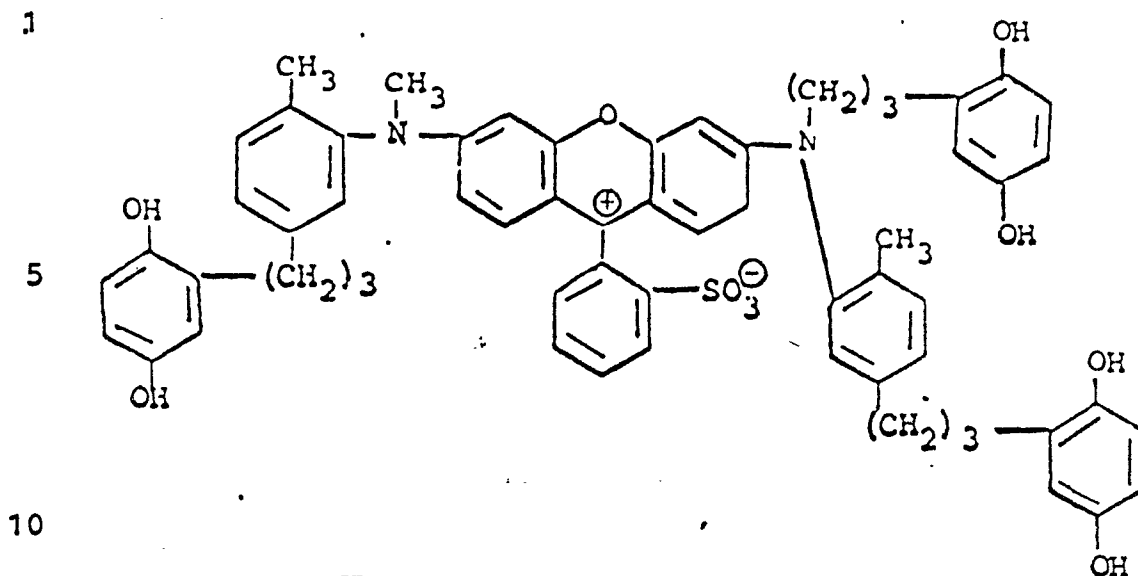
1. a layer of sodium cellulose sulfate coated at a coverage
of about 100 mg/m²;

15 2. a cyan dye developer layer coated at a coverage of about
635 mg/m² of the cyan dye developer described in Example I,
about 430 mg/m² of gelatin, about 237 mg/m² of N-dodecyl-
aminopurine and about 128 mg/m² of 4'-methyl phenyl hydro-
quinone;

20 3. a red sensitive silver iodobromide emulsion layer coated
at a coverage of about 1500 mg/m² of silver and about
900 mg/m² of gelatin;

25 4. an interlayer comprising about 1264 mg/m² of the penta-
polymer described in Example I and about 67 mg/m² of poly-
acrylamide;

30 5. a magenta dye developer layer coated at a coverage of
about 646 mg/m² of a magenta dye developer represented by
the formula



and about 323 mg/m² of gelatin;

15 6. a green-sensitive silver iodobromide emulsion layer coated at a coverage of about 1300 mg/m² of silver and about 596 mg/m² of gelatin;

20 7. an interlayer comprising about 950 mg/m² of the pentapolymer described in Example I and about 50 mg/m² of polyacrylamide;

25 8. a yellow dye developer layer coated at a coverage of about 820 mg/m² of the yellow dye developer described in Example I, and about 328 mg/m² of gelatin;

9. a spacer layer comprising about 150 mg/m² of N-dodecylaminopurine and about 150 mg/m² of gelatin;

30 10. a blue sensitive silver iodobromide emulsion layer coated at a coverage of about 1200 mg/m² of silver, about 421 mg/m² of gelatin and about 320 mg/m² of 4' methyl phenyl hydroquinone; and

35 11. a topcoat layer comprising about 484 mg/m² of gelatin.

1 The image-receiving element comprised a transparent base having coated thereon in succession:

1. a polymeric acid layer as described in Example V.
- 5 2. a timing layer comprising about 2570 mg/m² of the pentapolymer described in Example I and about 206 mg/m² of polyacrylamide;
3. a polymeric image receiving layer as described in
10 Example V with the exception that the coverages of the ether and the mixture of graft copolymer (PVA-P-4-VP) were 103 mg/m² and 2990 mg/m² respectively;
4. a topcoat layer comprising about 721 mg/m² of a polyoxyethylene-polyoxypropylene block copolymer (Pluronic
15 F-127[®], commercially available from BASF Wyandotte Co.) and about 309 mg/m² of polyvinylalcohol.

20 The control film unit was processed with a processing composition as described in Example V.

Three additional film units (VIA-VIC) were prepared and processed in the same manner with the exception that the processing composition further included 0.05 % of PMT,
25 compound I and compound II respectively. The results are shown in Table VIII.

TABLE VIII

30 Film Unit	D _{max}			D _{min}			Rel. Speed		
	R	G	B	R	G	B	R	G	B
Control	1.80	2.24	1.65	0.21	0.21	0.18	1.41	1.37	1.64
VI A	1.75	2.23	2.20	0.23	0.25	0.76	1.29	1.03	*
VI B	1.75	2.24	1.98	0.22	0.20	0.18	1.39	1.38	1.44
VI C	1.81	2.27	2.06	0.23	0.22	0.19	1.34	1.33	1.27

35 * blue relative speed too slow to measure

1 It is seen that the presence of PMT caused a large increase
in the blue D_{\min} and a very large decrease in the blue speed,
thus indicating that the PMT restrained development of the
blue sensitive silver halide emulsion prematurely. The
presence of compounds I and II provided an increase in the
5 blue D_{\max} without any increase in the blue D_{\min} .

EXAMPLE VII

As a control a film unit was prepared as follows: the photo-
10 sensitive element comprised a subcoated transparent poly-
ethylene terephthalate photographic film base having coated
thereon the following layers in succession:

1. a layer of sodium cellulose sulfate coated at a coverage
15 of about 14.4 mg/m²;

2. a cyan dye developer layer comprising about 747 mg/m² of
the cyan dye developer illustrated in Example I, about
1554 mg/m² of gelatin, about 270 mg/m² of 2-phenylbenzimid-
20 azole and about 68 mg/m² of 4'-methylphenylhydroquinone;

3. a red-sensitive silver iodobromide emulsion layer coated
at a coverage of about 1280 mg/m² of silver and about
768 mg/m² of gelatin;

25 4. an interlayer comprising about 2505 mg/m² of the penta-
polymer described in Example I and about 78 mg/m² of poly-
acrylamide;

30 5. a magenta dye developer layer comprising about 646 mg/m²
of the magenta dye developer described in Example I, about
452 mg/m² of gelatin and about 229 mg/m² of 2-phenyl-
benzimidazole;

- 1 6. a green-sensitive silver iodobromide emulsion layer coated at a coverage of about 510 mg/m² of silver and about 224 mg/m² of gelatin;
7. a spacer layer comprising about 1045 mg/m² of poly-
5 methylmethacrylate and about 55 mg/m² of polyacrylamide;
8. a green-sensitive silver iodobromide emulsion layer coated at a coverage of about 700 mg/m² of silver and about 336 mg/m² of gelatin;
- 10 9. an interlayer comprising about 1366 mg/m² of the pentapolymer described in Example I and about 87 mg/m² of polyacrylamide;
- 15 10. a yellow dye developer layer comprising about 820 mg/m² of the yellow dye developer illustrated in Example I, about 384 mg/m² of gelatin and about 208 mg/m² of 2-phenyl-benzimidazole;
- 20 11. a blue-sensitive silver iodobromide emulsion layer coated at a coverage of about 1280 mg/m² of silver, about 775 mg/m² of gelatin and about 306 mg/m² of 4'-methylphenylhydroquinone;
- 25 12. a top coat layer of about 484 mg/m² of gelatin.

The image-receiving element was identical to that described in Example V. The film unit was processed with a processing composition as described in Example V.

- 30 Six additional film units were prepared (VIIA-VIIF). Film Units VIIA-VIIC further included 1 mg/m², 2 mg/m² and 3 mg/m², respectively, of compound II in layer 5 of the photosensitive element and Film Units VIID-VIIF further
35 included 1 mg/m², 2 mg/m² and 3 mg/m² of compound XI in

1 layer 5 of the photosensitive element. An identical set of film units was also processed 35°C. The results are shown in Table IX.

TABLE IX

Film Unit	24°C					
	Dmax			Rel. Speed		
	R	G	B	R	G	B
Control	1.95	1.67	2.23	1.50	1.49	1.32
VII A	2.03	1.75	2.25	1.52	1.46	1.33
VII B	2.09	1.70	2.24	1.47	1.46	1.33
VII C	2.14	1.78	2.28	1.41	1.39	1.29
VII D	2.01	1.71	2.23	1.56	1.48	1.35
VII E	2.04	1.73	2.25	1.58	1.46	1.37
VII F	2.08	1.71	2.23	1.57	1.43	1.39
35°C						
Film Unit	Δ Dmax					
	R	G	B			
Control	-0.56	-0.20	-0.18			
VII A	-0.48	-0.19	-0.15			
VII B	-0.27	-0.09	-0.11			
VII C	-0.22	-0.06	-0.11			
VII D	-0.37	-0.12	-0.14			
VII E	-0.27	-0.05	-0.11			
VII F	-0.19	+0.06	-0.05			

It can be seen that at room temperature the presence of compounds II and XI provided an increase in red and green D_{max} . At 35°C processing the presence of compounds II and XI gave smaller losses (varying with the coverages) of red, blue and green D_{max} .

1

EXAMPLE VIIIPREPARATION OF COMPOUND XII

A catalyst was prepared by stirring a mixture of Celite[®] (10 g) (diatomaceous earth available from Johns Manville) and potassium fluoride dihydrate (15 g) in 250 ml of distilled water for 30 minutes. The water was removed on a rotary evaporator and the solids dried overnight at room temperature under high vacuum. The catalyst was further dried in a vacuum oven at 58-60°C for about two days.

To a stirred solution of 1-(4-hydroxyphenyl)-5-mercaptotetrazole (5 g) in dry tetrahydrofuran (50 ml) at room temperature under nitrogen there were added methylvinylsulfone (2,8 g) and the potassium fluoride/Celite[®] catalyst (1 g). The reaction mixture was stirred slowly for 24 hours. The solids were removed by filtration and the solvent was removed from the filtrate leaving behind a clear yellow-brown oil. The oil was dried under vacuum to give a tacky gum-like material. Recrystallization from methanol followed by drying to constant weight under vacuum gave a white, solid, compound XII, m.p. 139°-141°C.

The NMR spectrum of the material was consistent with compound XII. ¹³C NMR (dmso-d₆); δ 159.28, 153.69, 126.28, 124.05, 116.23, 53.01, 40.59, 25.29 ppm.

EXAMPLE IX

30

PREPARATION OF COMPOUND XIII

To a suspension of compound IV (2.166 g, 8.43 mmol) in methanol (10 ml) there were added, under nitrogen, 78 % methyl vinyl sulfone (1.44 g, 8.42 mmol) and 0.25 ml of 40 % benzyl trimethyl ammonium hydroxide in methanol and

1 the reaction mixture refluxed for twenty-four hours. The cooled reaction mixture was filtered to collect the white crystals which had formed. Thin layer chromatography showed that some starting materials were present. The desired product, compound XIII, was separated by column chromatography followed by removal of the solvent, crystallization on standing and drying. The structure of the product was confirmed by UV and ^{13}C NMR spectra.

EXAMPLE X

10

PREPARATION OF COMPOUND XIV

A catalyst was prepared by stirring a mixture of 10 g of Celite $\text{\textcircled{R}}$ (diatomaceous earth available from Johns Manville) and 15 g of potassium fluoride in 250 ml of distilled water for about 30 minutes, removing the water on a rotary evaporator at 56°C and drying the solid under vacuum at $58^\circ\text{--}60^\circ\text{C}$ to calculated weight, 196 g. The catalyst (1 g) was added to a stirred solution of 5 g of compound I and 1.8 g of methyl vinyl ketone in 50 ml of dry tetrahydrofuran, and the suspension was stirred under nitrogen at room temperature for three days. The solids were removed by filtering and the solvent removed from the filtrate to give about 7 g of a brown-yellow oil which was stirred briefly with 70 ml of ether at room temperature. The ether solution was decanted from the brown oily solid which had deposited, and the crystalline solid which formed in the ether on standing collected by filtration, washed and dried to give 4 g of white crystals (compound XIV), m.p. $118^\circ\text{--}120^\circ\text{C}$. The structure of the product was confirmed by a ^{13}C NMR spectrum.

35

1

EXAMPLE XIPREPARATION OF COMPOUND XV

A mixture of compound IV (257 mg, 1.0 mmol), methyl vinyl
5 ketone (0.081 ml, 1.0 mmol) and 200 mg of potassium fluoride
on Celite ^(R) catalyst (6 mmol/g) in about 2 ml of pyridine
was stirred overnight. The reaction mixture was poured into
5 % hydrochloric acid and the solid collected by filtration.
Thin layer chromatography showed two compounds. The desired
10 product (compound XV) was separated by column chromatography,
followed by removal of the solvent, crystallization
on standing and drying. The structure of the product was
confirmed by a proton NMR spectrum.

15

EXAMPLE XIIPREPARATION OF COMPOUND XVI

A stirred mixture of compound I (30.0 g, 0.154 m), 3-bromo-
20 propionitrile (20.72 g, 0.154 m) and sodium bicarbonate
(12.98 g, 0.154 m) in 600 ml of dry acetonitrile was heated
under nitrogen at 55°C for 42 hours, then cooled in an ice
bath and vacuum filtered. The filtrate was evaporated on a
rotary evaporator at 25°C. The syrupy residue was taken up
25 in 500 ml of ethyl acetate, washed with 400 ml of saturated
NaHCO₃ solution and twice with 200 ml of water, dried over
sodium sulfate and adsorptive activated carbon, and vacuum
filtered through diatomaceous earth. The filtrate was
evaporated on a rotary evaporator at 25°C and the crystall-
30 ine residue was taken up in 200 ml of ethyl acetate and
100 ml of hexane added to the solution. The solution was
stored in a refrigerator overnight and 50 ml of hexane
added. The crystalline material was collected by filtration,
washed with two 50 ml volumes of hexane and dried under
35 reduced pressure at ambient temperature to give 25 g
(65.7 % yield) of compound XVI.

1

EXAMPLE XIIIPREPARATION OF COMPOUND XVII

A mixture of compound II (11.647 g, 49.58 mmol), β -bromo-
5 propionitrile (6.626 g, 49.58 mmol) and sodium bicarbonate
(4.17 g, 49.58 mmol) in 200 ml of dry acetonitrile was
magnetically stirred in a 55°C bath under nitrogen overnight.
The reaction mixture was vacuum filtered and the filtrate
was stripped of solvent by rotary evaporation giving an
10 orange oily residue. The residue was taken up in ethyl
acetate (75 ml) and to the solution there were added seed
crystals and 150 ml of hexane. The mixture was scratched
and stored overnight in a refrigerator. The crystals which
formed were collected by filtration, washed twice with
15 hexane and dried to give 12.74 g of compound XVII as light
yellow crystals, m.p. 111°-113°C. The structure of the
product was confirmed by IR, UV and NMR spectra and thin
layer chromatography.

20

EXAMPLE XIIPREPARATION OF COMPOUND XVIII

A mixture of compound I (4.14 g, 21.3 mmol), p-acetoxybenzyl
25 chloride (3.94 g, 21.3 mmol) and sodium bicarbonate (1.79 g,
21.3 mmol) in 130 ml of dry acetonitrile was magnetically
stirred under dry nitrogen at 55°C overnight. The reaction
mixture was cooled in an ice bath, the solids removed by
vacuum filtration and the solvent stripped from the
30 filtrate to give an oily residue. The oily residue was
taken up in 100 ml of ethyl acetate, washed with 80 ml of
saturated sodium bicarbonate and twice with 80 ml of water,
dried over sodium sulfate and activated charcoal and the
mixture vacuum filtered through diatomaceous earth to give
35 a light yellow solution. The solvent was stripped from the

1 solution by rotary evaporation to give 12.5 g of a light
yellow oil. The oil was taken up in a mixture of 20 ml of
ethyl acetate and 80 ml of hexane and the solution allowed
to stand in a refrigerator overnight. The solvent was
stripped by rotary evaporation to give an oily residue
5 which was taken up in 100 ml of hexane and allowed to stand.
The crystals which formed were collected by filtration,
recrystallized from a mixture of 100 ml of hexane and 10 ml
of ethyl acetate, washed with 20 ml of hexane and dried to
give 6.17 g of the desired product (compound XVIII), m.p.
10 153°-154°C (84.6 % yield). The structure of the product was
confirmed by IR, UV and NMR spectra and thin layer chromato-
graphy.

EXAMPLE XV

15

As a control a film unit was prepared as follows: the
negative element comprised an opaque subcoated polyethylene
terephthalate film base on which the following layers were
coated in succession.

20

1. as a polymeric acid layer approximately 9 parts of a
1/2 butyl ester of polyethylene/maleic anhydride copolymer
and 1 part of polyvinyl butyral coated at a coverage of
about 26,460 mg/m²;

25

2. a timing layer comprising about 97 % of a 60-29-6-4-0.4
pentapolymer of butylacrylate, diacetone acrylamide,
methacrylic acid, styrene and acrylic acid and about 3 %
polyvinylalcohol coated at a coverage of about 3000 mg/m²;

30

3. a cyan dye developer layer comprising about 511 mg/m²
of the cyan dye developer described in Example I, about
70 mg/m² of 4-methyl phenyl hydroquinone and about 317 mg/
m² of gelatin;

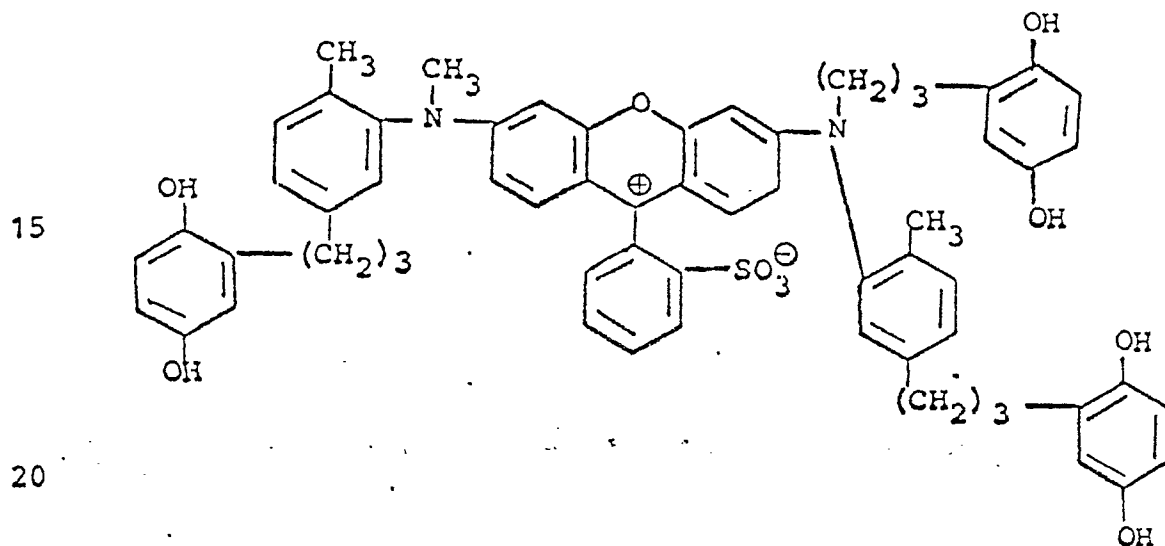
35

4. a red-sensitive silver iodobromide emulsion layer comprising about 1378 mg/m² of silver and about 827 mg/m² of gelatin;

5. an interlayer comprising about 2090 mg/m² of the pentapolymer described in layer 2, about 110 mg/m² of polyacrylamide and about 44 mg/m² of succinaldehyde;

6. a magenta dye developer layer comprising about 460 mg/m² of a magenta dye developer represented by the formula

10



20

and about 210 mg/m² of gelatin;

25

7. a green-sensitive silver iodobromide emulsion layer comprising about 723 mg/m² of silver and about 318 mg/m² of gelatin;

30

8. an interlayer comprising about 1881 mg/m² of the pentapolymer described in layer 2 and about 99 mg/m² of polyacrylamide;

35

9. a yellow dye developer layer comprising about 689 mg/m² of the yellow dye developer described in Example I and about 276 mg/m² of gelatin;

- 1 10. a blue-sensitive silver iodobromide emulsion layer comprising about 764 mg/m² of silver, about 499 mg/m² of gelatin, and about 265 mg/m² of 4'-methyl phenyl hydroquinone; and
- 5 11. a topcoat layer of about 400 mg/m² of gelatin.

The image-receiving element comprised a transparent sub-coated polyethylene terephthalate film base upon which there was coated an image-receiving layer coated at a coverage of
 10 about 3229 mg/m² of: (a) 3 parts of a mixture of 2 parts polyvinyl alcohol and 1 part poly-4-vinylpyridine and (b) 1 part of a graft copolymer comprised of 4-vinylpyridine (4VP) and vinyl benzyl trimethyl ammonium chloride (TMQ) grafted onto hydroxyethyl cellulose (HEC) at a ratio
 15 HEC/4VP/TMQ of 2.2/2.2/1; and about 53.8 mg/m² of 1,4-butanediol diglycidyl ether.

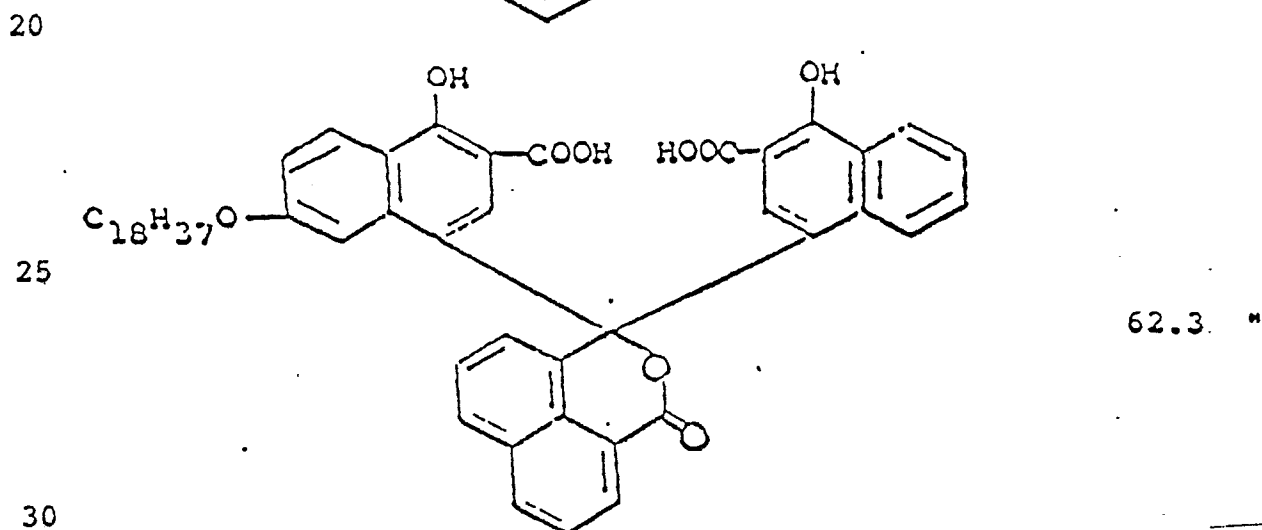
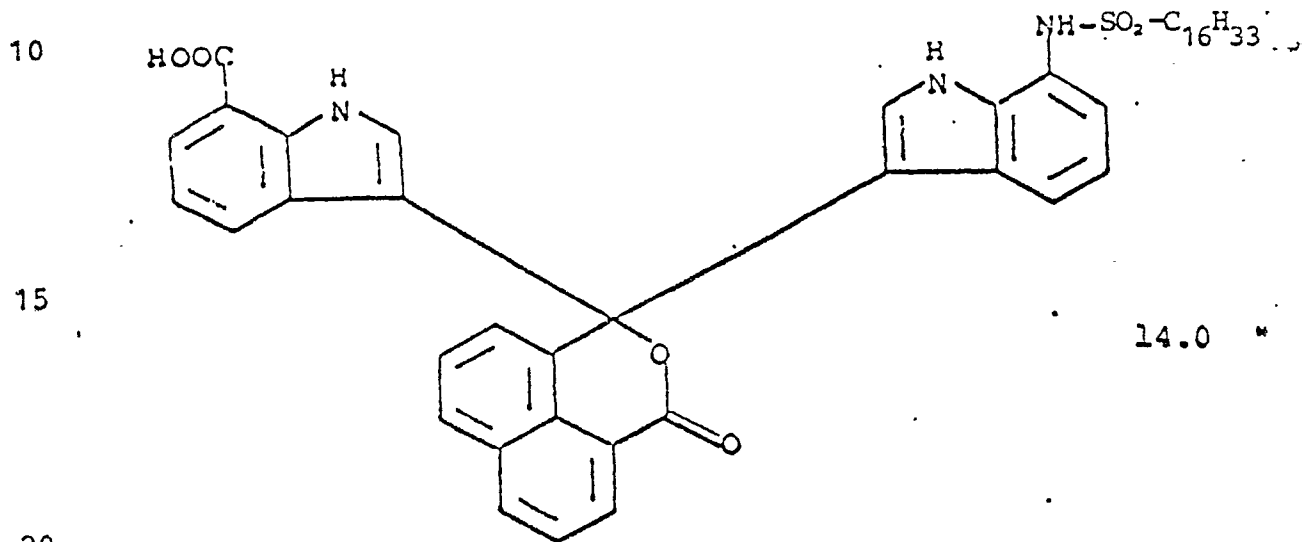
The film unit was processed with a processing composition made up as follows:

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Water	1632 ml.
TiO ₂	2312.0 grams
Oximated polydiacetoneacrylamide	32.0 "
25 Potassium hydroxide (45% solution)	468.0 "
Benzotriazole	22.0 "
4-aminopyrazole-(3,4-d)pyrimidine	10.0 "
6-methyl uracil	12.0 "
30 N-hydroxyethyl-N,N',N'-triscarboxymethyl ethylene diamine	30.0 "
Polyethylene glycol (M.W. 4000)	18.0 "

35

1	Bis(20aminoethyl)sulfide	0.8	"
	Colloidal silica (30% solids)	37.0	"
	N-phenethyl- α -picolinium bromide (50% solids)	102.0	"
5	Allopurinol	3.3	"
	2-methyl imidazole	23.8	"
	6-methyl-5-bromo azabenzimidazole	4.8	"



The negative element was exposed (2 meter-candle-seconds)
 on a sensitometer to a test exposure scale with white light,
 and then brought together with the image-receiving element
 and processed at room temperature (24°C) by passing the

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1 film unit through a pair of rollers set at a gap spacing of
 about 0.066 mm. The film unit was kept intact and viewed
 through the base of the image-receiving element.

5 An identical film unit was processed in the same manner at
 35°C. The neutral density columns of the images were read
 on a densitometer to obtain the D_{\max} and D_{\min} values for red,
 green and blue, respectively. The values obtained are shown
 in Table IX.

10 Seven additional film units according to the invention
 (VIII A - VIII G) were prepared. These were identical to the
 control with the exception that the negatives also included
 a topcoat layer comprising about 215 mg/m² of a blocked
 compound according to the invention (as shown in Table IX)
 15 and about 215 mg/m² of gelatin. The film units were pro-
 cessed as described above at 24°C and at 35°C. The results
 are shown in Table X.

20

TABLE X

Film Unit	Com- Pound	24°C					
		D _{max}			D _{min}		
		R	G	B	R	G	B
Control		1.81	1.60	1.31	0.15	0.16	0.24
25 VIII A	XII	1.60	1.48	1.40	0.18	0.17	0.24
VIII B	XIII	1.33	1.43	1.41	0.15	0.16	0.23
VIII C	XIV	1.68	1.74	1.91	0.16	0.17	0.26
VIII D	XV	1.44	1.39	1.37	0.16	0.13	0.16
VIII E	XVI	1.30	1.42	1.46	0.15	0.13	0.15
30 VIII F	XVII	1.58	1.65	1.64	0.16	0.13	0.15
VIII G	XVIII	1.48	1.83	1.88	0.14	0.15	0.23

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1 table X (continued)

Film Unit	Com-Pound	35°C					
		D _{max}			D _{min}		
		R	G	B	R	G	B
Control	-	1.43	1.20	0.95	0.16	0.17	0.25
5 VIIIA	XII	1.32	1.23	1.12	0.16	0.17	0.24
VIIIB	XIII	1.07	1.13	1.11	0.16	0.17	0.25
VIIIC	XIV	1.65	1.67	1.62	0.16	0.17	0.26
VIIID	XV	1.28	1.24	1.14	0.16	0.14	0.17
VIIIE	XVI	1.24	1.27	1.24	0.17	0.14	0.17
10 VIIIF	XVII	1.40	1.35	1.34	0.16	0.14	0.17
VIIIG	XVIII	1.67	1.78	1.61	0.14	0.15	0.25

It is seen that at both 24°C and 35°C the blue D_{max} of Film Units VIIIA - VIIIG is higher than that of the Control and, in some instances much higher. At 24°C the green D_{max} of Film Units VIIC, VIIF and VIIIG is higher than that of the Control while at 35°C the green D_{max} of all the Film Units except VIIIB is higher.

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EXAMPLE XVIPREPARATION OF COMPOUND XIX

A mixture of compound II (1.175 g, 5 mmol), sodium bicarbonate (420 mg, 5 mmol) and p-acetoxybenzyl chloride (925 mg, 5 mmol) in 30 ml of acetone was heated to boiling on a steam bath for 24 hours. The solution was vacuum filtered and the solvent was removed from the filtrate by rotary evaporation at 25°C to give a light yellow oil. The oil was taken up in 30 ml of methanol, the solution vacuum filtered and the filtrate allowed to stand overnight in a refrigerator. The light yellow crystals which formed were collected by filtration and dried under reduced pressure at room temperature to give 1.34 g (70 % yield) of compound XIX, m.p. 126-127°C.

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1 $C_{18}H_{17}N_5O_3S$ requires 56.38 % C, 4.47 % H, 18.27 % N and
8.36 % S. Elemental analysis found 56.50 % C, 4.57 % H,
18.27 % N and 8.12 % S.

Although the invention has been described with respect to
5 specific preferred embodiments, it is not intended to be
limited thereto but rather those skilled in the art will
recognize that variations and modifications may be made
within the spirit of the invention and the scope of the
appended claims.

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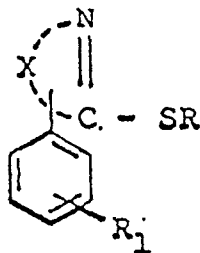
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CLAIMS

1. A photographic product for use in forming a diffusion transfer photographic image comprising a photosensitive element comprising a support carrying at least one silver halide emulsion layer having associated therewith an image dye-providing material, a second sheet-like element positioned in superposed or superposable relationship with said photosensitive element, an image receiving layer positioned in one of said elements, means for lowering the pH of an aqueous alkaline processing composition positioned in one of said elements, a rupturable container releasably holding an aqueous alkaline processing composition adapted, when distributed between a pair of predetermined layers carried by said photosensitive element and said second element, to develop said silver halide emulsion and provide a diffusion transfer image on said image receiving layer, characterized in that said product includes at least one compound represented by the formula

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wherein X represents the nonmetallic atoms necessary to form a nucleus which completes a 5- or 6-membered heterocyclic moiety on said structure, R is H, an alkali metal or a group which is cleavable in said aqueous

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alkaline processing composition and R_1 is
either a group which has a pKa of from about
7 to about 14 which is ionizable to an anion
and wherein the silver salt of the mercaptan
35 resulting from cleavage or ionization of -SR
is more soluble in said aqueous alkaline
processing composition in the pH range within
which R_1 is ionized to an anion than said
silver salt is below that pH range or a
40 precursor,

wherein said processing composition initially
has a pH substantially equal to or above
the pKa of R_1 and said means for lowering
the pH of an aqueous alkaline processing
45 composition is adapted to lower the pH of
said aqueous alkaline processing composition
below the pKa of R_1 .

2. A product according to Claim 1 wherein the
photosensitive element comprises a support
carrying a blue-sensitive silver halide
emulsion layer having a yellow image dye-
5 providing material associated therewith, a
green-sensitive silver halide emulsion layer
having a magenta image dye-providing material
associated therewith and a red-sensitive
silver halide emulsion layer having a cyan
10 image dye-providing material associated
therewith.
3. A product according to any preceding claim
wherein said image dye-providing materials
are dye developers and said emulsions are
negative working emulsions.

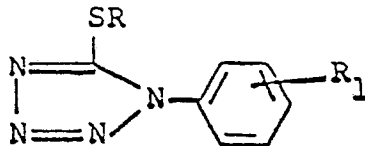
4. A product according to any preceding claim wherein said compound is incorporated in said processing composition.
5. A product according to Claim 4 wherein said compound is present in an amount of from about 0.02 to about 0.07 percent by weight of said processing composition.
6. A product according to any preceding claim wherein said second element has a transparent support and includes said means for lowering the pH of an aqueous alkaline processing composition and further includes means for providing a layer of light-reflecting pigment between said image-receiving layer and said silver halide emulsion layer(s).
7. A product according to Claim 6 wherein said light-reflecting pigment is titanium dioxide.
8. A product according to any preceding claim wherein R is H.
9. A product according to any preceding claim wherein R_1 is selected from the group consisting of $\begin{array}{c} \text{N-OH} \\ || \\ -\text{C}-\text{CH}_3 \end{array}$, -OH, and $-\text{SO}_2\text{NH}_2$.
10. A product according to any of claims 1 to 7 or 9 wherein R is a group which is cleavable in said aqueous alkaline processing composition and said compound is incorporated in said photosensitive element.

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11. A product according to Claim 10 wherein R is $-\text{CH}_2\text{CH}_2\text{SO}_2\text{R}_5$ wherein R_5 is alkyl, aryl or substituted aryl.
12. A product according to any preceding claim wherein said compound is represented by the formula



13. A product according to any of claims 1 to 11 wherein said compound is represented by the formula...



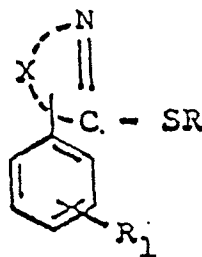
14. The product as defined in Claim 15 wherein R is H or $-\text{CH}_2-\text{CH}_2\text{SO}_2\text{R}_5$, R_5 is alkyl, aryl or substituted aryl and R_1 is selected from the group consisting of $-\text{C}(\text{N}=\text{OH})-\text{CH}_3$, $-\text{OH}$ and $-\text{SO}_2\text{NH}_2$.

15. A product according to any of claims 1 to 7 wherein said compound is incorporated in said processing composition and in said photosensitive element, R is H for said compound incorporated in said processing composition and R is a group which is cleavable in said aqueous alkaline processing

composition for said compound which is incorporated in said photosensitive element.

16. A diffusion transfer photographic process comprising exposing a photographic product including photosensitive element comprising a support carrying at least one silver halide emulsion layer having associated therewith an image dye-providing material and an aqueous alkaline processing composition, applying said aqueous alkaline processing composition to said exposed photosensitive element to effect development and to form an imagewise distribution of image dye-providing material as a function of development and transferring at least a portion of said imagewise distribution of image dye-providing material to an image receiving layer in superposed or superposable relationship therewith to thereby provide a diffusion transfer image, characterized in that said photographic product comprises a product according to any of claims 1 to 15.

17. A compound of the formula



- wherein X represents the nonmetallic atoms necessary to form a nucleus which completes a 5- or 6-membered heterocyclic moiety, R is


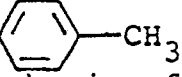
a group which is cleavable in aqueous alkaline medium by hydrolysis, by quinone methide elimination, by hydrolysis followed by quinone methide elimination or by beta-
 10 elimination and R_1 is either a group which has a pKa of from about 7 to about 14 which is ionizable to an anion and wherein the silver salt of the mercaptan resulting from cleavage of $-SR$ is more soluble in the pH
 15 range within which R_1 is ionized to an anion than it is below that pH range, or a precursor thereof.

18. A compound according to claim 17 wherein R is $-(CH_2)_2SO_2R_5$ where R_5 is alkyl, aryl or substituted aryl.

19. A compound according to claim 18 wherein R_5 is alkyl having from 1 to 6 carbon atoms.

20. A compound according to any of claims 17 to

19 wherein R_1 is $-OH$, $-O-C(=O)-CH_3$, $-C(=O)-CH_3$,

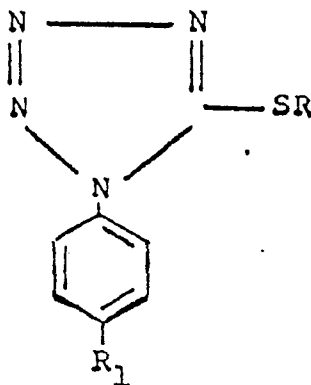
$-SO_2NH_2$, $-SO_2NHCH_3$, $-SO_2NHC_8H_{17}$, $-SO_2NH-$ ,
 $-NHSO_2CH_3$, $-NHSO_2-$  $-CH_3$ or $-C(=O)-Z$,

5 where Z is H, alkyl having from 1 to 10 carbon atoms, aralkyl, phenyl or substituted phenyl.

21. A compound according to any of claims 17 to 20 wherein X represents the nonmetallic atoms necessary to complete a tetrazole moiety.

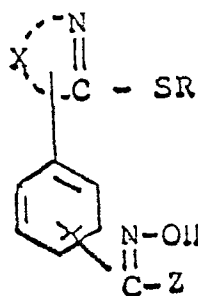
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22. A compound according to claim 21 which is represented by the formula



where R_1 is $-OH$, $\begin{matrix} N-OH \\ || \\ -C-CH_3 \end{matrix}$ or $-SO_2NH_2$.

23. A compound of the formula



wherein X represents the nonmetallic atoms necessary to form a nucleus which completes a 5- or 6-membered heterocyclic moiety, R is H , an alkali metal or a group which is cleavable in aqueous alkaline medium and Z is H , alkyl having from 1 to 10 carbon atoms, aralkyl, phenyl or substituted phenyl.

24. A compound according to Claim 23 wherein Z is alkyl having from 1 to 10 carbon atoms.

25. A compound according to claims 23 or 24
wherein R is $-\text{CH}_2-\text{CH}_2-\text{SO}_2-\text{R}_5$ is alkyl or aryl.

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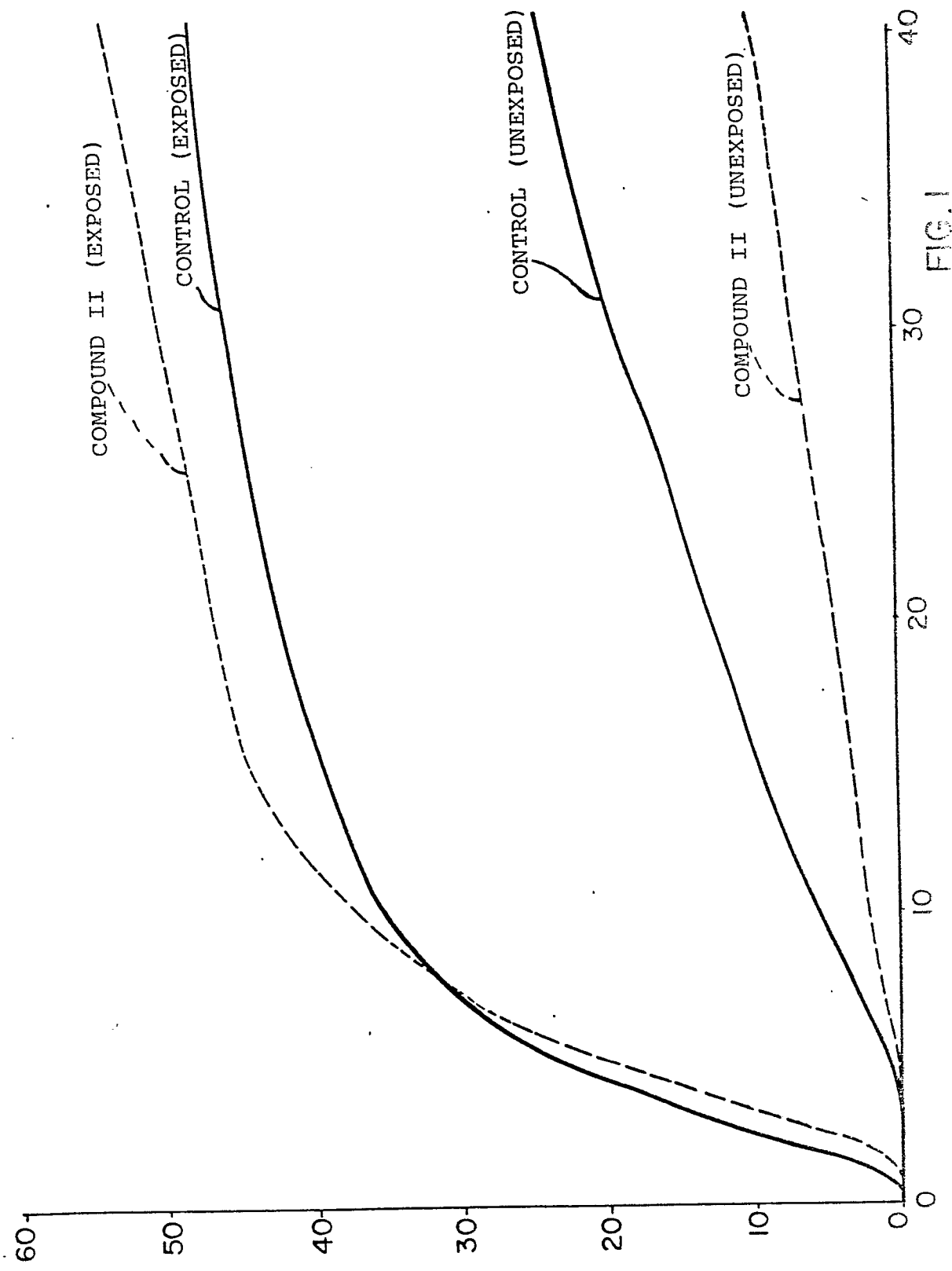


FIG. 1