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- A process for preventing from discoloring and fading of dye image.
- A process for reducing or preventing a dye image in a color image froming material, or a dye image in a colored print, from discoloring and/or fading is described which comprises forming a colordevelopable leuco dye which develops color under the action of heat and/or light either in said color image forming material, or upon exposure of said image forming material, or in said colored print.

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A PROCESS FOR PREVENTING FROM DISCOLORING AND FADING OF DYE IMAGE

The present invention relates to a process for preventing from discoloring and fading a dye image in a color image forming material or printed matter.

Generally, an image made of dye or dyestuff,

5 in printed matter such as a color print or a poster,
is observed or displayed under conditions of strong
illumination by sunlight or by the light of an
illuminator. If this illumination lasts many hours,
the image is discolored or faded by the illuminating
10 light giving poor color-balance or color-reproductivity.

However, even with those not always being illuminated by the light but preserved for most of the time in the dark such as a color movie film, a color slide, a color negative film, a color print 15 pasted in an album, it is known that image discoloration and fading occur on storage. The former phenomenon is called light discoloration and fading while the latter is called dark discoloration and fading. With the object of preventing an image from discoloring and 20 fading, there have been proposed processes such as those in which, for example, a dye or dyestuff having improved resistance to discoloration and fading by having a different chemical structure is used, or in which a discoloration and fading preventive agent, or 25 a coloring and fading preventive bath, is used with a conventional type of dye or dyestuff.

Besides these, many processes are known in which an ultra-violet ray absorbant is added in the neighborhood of the dye or dyestuff because light

discoloration and fading are basically caused by the highly energized ultra-violet ray of normal light, or a type of oxidation inhibitor is used because such discoloration and fading are governed by an oxidizing 5 atmosphere; examples of these are organic compounds having a phenolic hydroxyl group and derivatives thereof. For improving said dark discoloration and fading, there have been proposed processes which use a stabilizing bath containing a hydantoin compound, 10 a carbohydrazide compound, polymethylol compound, an organic bronzing preventive or the like to serve as a fading preventive, in which an ester phosphite compound, a benzotriazole derivative or the like is added to a photographic emulsion layer; or in which unreacted 15 coupler is eliminated.

With these conventional processes for improving said discoloration and fading it is rather difficult to show that satisfactory effects are always obtained; further, when using an auxiliary 20 additive such as a discoloration and fading preventive agent or a discoloration and fading preventive bath, the difficulties involving manufacture and processing are increased; also they tend to have a bad physical or photographic influence on the image surface that 25 results; for example it can be a sticky, a rough or a soiled image surface, so that there is still considerable room for improvement at the present time.

As the result of thorough studies, we have found, according to the present invention, a process 30 for preventing from discoloring and/or fading a dye image formed in color image forming material or of a dye image formed in a printed matter, the improvement comprising forming a color-developable leuco dye which develops a color by light or heat in said color image forming material or in said printed matter.

In other words, according to the present invention, a color compensation process is provided in which the apparent color density of the image may be constantly maintained over a long period of time 5 by the material already containing a compound which gradually develops color on being exposed to light or heat, which causes discoloring and fading of said color image formed by a conventional type of dye or dyestuff. Also, in the case of light discoloration 10 and fading, it is not only possible to maintain the apparent density constant for a long period of time by using a compound which develops color gradually on being exposed at least to light, in a layer on the light illuminated side or the light reflected 15 side of the layer(s) containing the usual dyes or dyestuffs, but also it is possible to prevent normal types of dyes or dyestuffs from discoloring and fading because said compound can act as a light filter for the dye or dyestuff.

20 In the invention, the active substance is a leuco dye. In broad sense, a leuco dye is a generic name for an organic dye capable of changing its color-tone on oxidation-reduction or vice versa; those of the reduction type are colorless or light-colored, 25 while those of the oxidation type are deep-colored. The dyes of the reduction type are so-called "leuco dyes" as opposed to the normal oxidation type of dyes. In the invention, however, it is not always necessary that said dye forming reaction should be reversible. 30 For image forming materials using a light- or heat-colordevelopable leuco dye, as described in, for example, Japanese Patent Applications Nos 28530/1980 and 121427/1980, fading prevention processes as the process of this invention are not known.

In order to effectively prevent a normal dye or dyestuff from discoloring and fading by making use of a light- or heat-developable leuco dye, it is preferable for the light- or heat-color-developable leuco dye to be present imagewise in the same way as the normal dye or dyestuff is present, or to be formed imagewise.

For example, when the leuco dye is used in a color image forming material such as a photographic 10 material, and in order to make said light— and heat—color—developable leuco dyes form imagewise according to the light—information, it is necessary that at least three types of substances should co—exist, i.e. a coupler that is a compound forming a leuco dye, a 15 developer and a compound having a selective oxidation function in relation to the light information.

Also, for example, when a leuco dye is used in printed matter, it is possible to produce an image in which the yellow, magenta, cyan and black (i.e. 20 a black dye) components are each multiprinted imagewise, and said image can be prevented from discoloring and fading by multiprinting imagewise on any layer a leuco dye in which a color is developed by light or heat, or the three substances, that is, a coupler 25 forming said leuco dye, a developer and an oxidizer.

In the invention, the leuco dyes having a fading preventive function may be any leuco dye which develops color by light or heat, and <u>inter alia</u>, in particular a developer having a sulfonamide group and a 30 coupler therefor.

The developers having a sulfonamide group which can be used in the invention include those having the formula:

Au-Co-NH-SO2-Y

wherein Au represents an auxochrome i.e. an electron emitting (donating) group such as a group having a lone electron-pair or an aliphatic group which 5 makes the electron mobility easier by interaction with π electron of a chromophore (i.e. an atomic group having an unsaturated coupling); in general said auxochrome has a bathochromic effect and a hyperchromic effect. Examples thereof are -R, -OR, -NRR' 10 halogen, wherein R and R' independently represent H or an alkyl group having one to eight carbon atoms such as a methyl group, an ethyl group and a propyl group; or a substituted alkyl group such as β -hydroxyethyl group, β -methoxyethyl group and a β -methylsulfonamido-15 ethyl group; further in the case of -NRR', R and R' may together form with the nitrogen atom a nitrogencontaining saturated hetero ring such as a morpholinyl group, piperidyl group, 3-hydroxy piperidyl group, piperazyl group, pyrolidyl group, imidazolidyl group 20 or piperazolidyl group.

Co represents a group having at least one conjugated double bond such as a butadienylene group, phenylene group, a substituted phenylene group and preferably phenylene group or a substituted 25 phenylene group.

Y represents a group by which said developer or said leuco dye is endowed with suitable properties, of, say, stability, diffusibility and dissolvability.

Examples include a hydroxy group, or a salt 30 thereof such as -ONa; an alkyl group having from 1 to 7 carbon atoms such as a methyl group or a butyl group; an amino group such as N,N-dimethylamino group; or an

aryl group such as a phenyl, tolyl, 4-methoxyphenyl, 4-chlorophenyl, α -naphthyl or β -naphthyl group.

Concrete examples of developers having a sulfonamide group which can be used in the invention 5 are shown as follows:

B - 1

$$C\ell$$
 $HO \longrightarrow NH - SO_2 - N < CH_3$
 CH_3

B - 3

Br

$$HO \longrightarrow NH - SO_2 \longrightarrow CH_3$$

$$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \end{array} > \text{N} \longrightarrow \begin{array}{c} \text{NH} - \text{SO}_2 \longrightarrow \text{CH}_3 \\ \end{array}$$

5 B - 5
$$C_{2}H_{5} > N \xrightarrow{CH_{3}} NH - SO_{2} - N < CH_{3}$$

$$C_{2}H_{5} > N \xrightarrow{CH_{3}} NH - SO_{2} - N < CH_{3}$$

$$C_{2}H_{5}$$
 $NH-SO_{2}$

$$\begin{array}{c} B - 7 \\ C_2H_5 \\ C_2H_5 \end{array} N - \begin{array}{c} CH_3 \\ NH - SO_2 - CH_3 \end{array}$$

$$\begin{array}{c} B - 8 \\ C_2H_5 \\ C_2H_5 \end{array} > N \xrightarrow{CH_3} NH - SO_2 \xrightarrow{C}$$

B - 9
$$C_2H_5 > N \xrightarrow{CH_3} NH - SO_2 \xrightarrow{CCH_3} OCH_3$$

$$\begin{array}{c} C_2H_5 \\ C_2H_5 \\ \end{array} NH - SO_2 - OCH_3 \end{array}$$

$$\begin{array}{c} C_2H_5 \\ C_2H_5 \end{array} N \xrightarrow{CF_3} NH - SO_2 \xrightarrow{CCH_3} \\ \end{array}$$

5 B - 12
$$C_{2}H_{5}$$
 $NH - SO_{2} - N < CH_{3}$ CH_{3} CH_{3} CH_{3} CH_{3}

$$C_{2}H_{5}$$

$$C_{2}H_{5}$$

$$C_{2}H_{5}$$

$$NH - SO_{2} - CH_{3}$$

$$CH_{3}SO_{2}NHC_{2}H_{4}$$

$$B - 14$$

$$C_2H_5 > N - NH - SO_2 - NH$$

$$\begin{array}{c} C_2H_5 \\ \\ HOC_2H_4 \end{array} > N \xrightarrow{CH_3} \begin{array}{c} CH_3 \\ \\ NH-SO_2-N \\ \\ CH_3 \end{array}$$

$$\begin{array}{c} C_2H_5 \\ \\ HOC_2H_4 \end{array} > N \xrightarrow{CH_3} NH - SO_2 \xrightarrow{C}$$

B - 17
$$C_2H_5 \longrightarrow NH - SO_2 \longrightarrow C\ell$$

$$B - 18$$

$$C_2H_5$$
 $NH-SO_2$
 CH_3
 CH_3
 CH_3

$$5 B - 19$$

$$O \longrightarrow N \longrightarrow NH-SO_2-N < CH_3$$

$$0 N - N - NH - SO_2 - N$$

$$10 \qquad \qquad \boxed{N - NH - SO_2 - CH_3}$$

$$B - 23$$

$$B - 24$$

$$C_2^{H_5}$$
 $N - C_3^{CH_3}$ - NHSO₃Na

B - 25

B - 26
$$C_{2}^{H_{5}} N - OCH_{3} - NHSO_{2} - OCH_{3}$$

5 The above-mentioned developers having a sulfonamide group can easily be synthesized from a primary amine compound and a sulfonyl halide compound.

To serve as coupler in the present invention, any one of the well-known types used in silver halide 10 color photographic materials may be utilized. there can be used, as yellow couplers, for example, a benzoylacetoanilide compound as described in US Patent No 2 875 057, a pivaloylacetoanilide compound as described in US Patent No 3 265 506 or a carbamoylaceto-15 amide compound as described in Japanese unexamined patent publication No 154 631/79; as magenta couplers, for example, a 5-pyrazolone compound as described in US Patent No 2 600 788, a pyrazolotriazole compound as described in Belgian Patent No 792525, a pyrazolino-20 benzimidazole compound as described in US Patent No 3 061 432, an indazolone compound as described in Belgian Patent No 769116, a cyanoacetyl compound as described in US Patent No 2 338 677 or a thiazoline compound; and as cyan couplers, a phenol compound as described in

US Patent No 2 801 171, a diacylaminophenol compound or a naphthol compound as described in US Patent No 2 474 293, for example.

Besides the above, it is also possible to utilize a cycloactive methylene compound having at least one carbonyl group in the ring, such as an indanone compound, an indandione compound, a thionaphthenone compound, a cumaranone compound, a thioindoxyl compound, an isooxazolone compound, a pyrimidazolone 10 compound an oxyindole compound or a homophthalimide compound. In addition thereto, it is also possible to utilize the so-called active-site substituted couplers in which one of the hydrogen atoms of the active-sitemethylene group of the abovementioned coupler is 15 substituted by another elimination group such as a halogen atom or an alkoxy, aryloxy, heteroyloxy, sulfonyloxy, acyloxy, acyl, thiocyano, alkylthio, arylthio, heteroylthio, sulfonamide, sulfonyloxy or arylazo.

When a light- or heat-color-developable leuco dye is synthesized in advance by making use of a developer having a sulfonamide group and a coupler and the leuco dye thus synthesized is used in discoloring and fading prevention, the process for synthesizing said dye described in Japanese Patent Application No 28530/1980 can be utilized.

When a light- or heat-color-developable leuco dye is synthesized in advance, said leuco dye being present in a photographic sensitive material and then 30 formed imagewise, the dye should be able to co-exist with a compound having an oxidation function which operates selectively in accordance with the light information. Examples of such compounds having a selective oxidation function include polyhalogenated

hydrocarbons such as a tetrabromomethane or tribromophenylsulfone compound, a bis-imidazole compound,
a pyridine-N-oxide compound, an organic acid silver
compound or silver halide. In the invention, it is
advantageous to use a silver halide because it
amplifies a light information very well. Oxidation
is carried out by developing an exposed silver halide
and thereby a developer having said sulfonamide group
and a coupler are effectively converted into a leuco
10 dye.

When using said silver halide in the invention, it is also possible to use effectively a known cross oxidizer, for example an aminophenol compound, a phenylenediamine compound, a 3-pyrazolidone 15 compound, an azine compound or a bipyridium compound and the like. Examples of these are given below:

C - 1

c - 2

c - 3

C-4

5 C — 5

$$H_3C$$
 $N \longrightarrow N < CH_3$

0 - 6

$$N \longrightarrow N$$

c - 7

C - 8

10

$$\begin{array}{c}
 & H \\
 & N - C = 0 \\
 & C H_3
\end{array}$$

$$CH_3$$
 $N - C = 0$
 CH_3
 CH_2
 OH

$$C - 14$$

$$H^3C-N$$
 $N-CH^3$

Leuco dye formed from a developer having a sulfonamide group and a coupler creates a chromophore which develops color on exposure to light or heat such as ultraviolet rays, visible light or infrared rays. 5 Other color-developable leuco dyes which can be used are described in, for example, "Research Disclosure" vol 128, No 12838 and No 12839 and Ibid, vol 133, No 13313. Further, a leuco dye formed from a coupler having an elimination group such as an acetamide group, 10 trichloroacetamide group, an imide group at the active site of a pyrazolone magenta coupler (through a nitrogen atom) and a p-phenylene diamine color developer such as 4-(N-ethyl-N-β-hydroxyethylamino)-2-methylaniline or 4-(N,N-diethylamino)-2-methylaniline, which are frequen-15 tly used in normal color developing processes, can also be one of the compounds capable of developing color with light or heat and said leuco dye can be used in the present invention. It will be appreciated that the speed at which the leuco dyes are converted by light 20 or heat into the colored dyes, and the maximum absorption wavelength and the mole absorbance coefficient, for example, of the dyes thus formed depend inter alia on the size of the conjugated system; the nature of the chromophore; the nature of electron withdrawing group 25 and electron donating group of the auxochrome; the ionization and cyclization thereof; the degree of steric hindrance, hydrogen bonding or metallic complex formation in or between molecules caused by the presence of other substituents; and the dye medium.

With reference to a silver halide color photosensitive material, there should be present a coupler for forming a light- or heat-color-developable leuco dye and a developer containing said sulfonamide group, for example, besides the coupler for forming the normal dye image and the normal color developer.

The coupler for forming the normal dye image and the coupler for forming a light- or heat-color-developable leuco dye may be the same or different.

The layer in which the leuco dye is formed may also be either the same or different from the layer in which the normal dye image is formed; in this case, the silver halide in the normal dye image forming layer may be used also for forming the leuco dye, or silver halide may be present in another layer for the leuco dye.

The processes for including the developer and coupler used in this invention are not significant and it is possible to use all known processes for normal silver halide photosensitive materials.

Thus, for example, the coupler and the

15 developer may be dissolved in a solvent of high boiling
point to make fine oil-drops and said drops are dispersed,
as described in US Patent No 2 322 027; an antidiffusion group and water-soluble group may be coupled
thereto and the dissolution and dispersion thereof is

20 then carried out, as described in US Patent No 2 186 849;
they may be incorporated as a component of a macromolecular compound, as described in US Patent No 2 397 864;
they may be loaded onto a latex polymer, as described
in Japanese Patent Publication Open to Public

25 Inspection Nos 59942/1976 and 59943/1976; or they may be
dispersed mechanically by means of a colloid mill or
the like.

On the other hand, when the developers and couplers used in this invention are supplied from a 30 photographic processing liquid, it is preferable to introduce a suitable group for giving the respective compounds appropriate properties such as dissolvability,

permeability, diffusibility and the like, in consideration of the dissolvability of the developers and couplers to be used to a processing liquid or the permeability, diffusibility and the like thereof to a silver halide color photosensitive material.

The following Examples further illustrate the present invention:

Example 1

The following components were coated over to a triacetate cellulose film which had been sublayered with gelatin.

(Sample A)

	(24.1.2.1.2.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1	
5	Cyan Coupler:	
	2-[Y-(2,4-di-t-pentylphenoxy) butanamide]naphthol	1.3g/m ²
	Dioctyl phthalate	$0.9g/m^2$
10	Silver iodobromide (in Silver equivalence)	0.95g/m ²
	Ossein gelatin	$1.4g/m^2$
	Gelatin hardener (Bis-vinylsulfonyl methylether)	20mg/m ²
-	(Sample B)	•
15	Cyan Coupler:	
	2-[2-(2,4-di-t-pentylphenoxy) butanamide]-4,6-dichloro-5- methylphenol	1.lg/m ²
	Dioctyl phthalate	0.76g/m ²
20	Silver iodobromide (in Silver equivalence)	0.8g/m ²
	Ossein gelatin	$1.4g/m^2$
	Gelatin hardener (Bis-vinylsulfonyl methyl ether)	20mg/m ²
2 5	(Sample C)	
	Matter in which Exemplified Compound B-16 were contained in Sample A	0.23g/m ²
	(Sample D)	
30	Matter in which Exemplified Compound B-13 were contained in Sample B	0.24g/m ²

(Sample E)

Matter in which

Exemplified Compound B-16 $0.23g/m^2$ Exemplified Compound C-12 $140mg/m^2$

5 were contained in Sample A

(Sample F)

Matter in which

Exemplified Compound B-13 $0.24g/m^2$ Exemplified Compound C-12 $140mg/m^2$

10 were contained in Sample B.

The above samples were exposed to light through a step-wedge with 0.15 constant steps for 3.2 C.M.S. 1/60 sec, and the following processing steps using the following processing solutions were 15 carried out.

(Processing Steps)

(1)	Developing Bath	38°C	2 min.
(2)	Bleaching Bath	38°C	1 min.
(3)	Washing	38°C	3 min.
20 (4)	Fixing	38°C	5 min.
(5)	Washing	18 - 22°C	3 min.

With Samples A, C and E, Developer (A) was used.

Developer (A)

4- (N-ethyl-N-β-hydroxyethylamino)25 2-methylaniline sulfate

4.8 q

	Sodium sulfite, anhydrous	4.3 _. g
	Hydroxylamine · 1/2 sulfate	2.0 g
	Potassium carbonate	38.0 g
	Sodium bromide	1.3 g
5	Nitrilotriacetic acid 3 sodium salt, monohydrate	2.5 g
	Add potassium hydroxide and water to adjust the pH value to	pH 10.3
	and to make	1.0 ltr
10	With Samples B, D and F, Developer (B)	was used.
	Developer (B)	
	Benzyl alcohol	15 ml
	Ethylene glycol	13 m1
15	4-(N-ethyl-N- β -methylsulfonamide ethylamino)-2-methylaniline	3.7 g
	Hydroxylamino.1/2 sulfate	2.5 g
	Potassium sulfite	1.8 g
	Potassium bromide	0.7 g
	Potassium carbonate	25.0 g
20	4-4'-diaminostilbene disulfonate	0.8 g
	Adjust the pH value to	pH 10.3
	Add water to make	1 ltr.
	With further Samples E and F, Developer	(C) was
	used, respectively.	
25	Developer (C)	
	Potassium carbonate	38.0 g

	Potassium bromide	1.0 g
	Add water to make	1 ltr.
	[Composition of Bleaching Solution]	
5	Ethylenediamine tetraacetic acid iron ammonium salt	100.0 g
	Ethylenediamine tetraacetic acid diammonium salt	10.0 g
	Ammonium bromide	150.0 g
	Glacial acetic acid	10.0 ml
10	Add water to make	1 ltr.
	Adjust the pH value with aqueous ammonia to	рн 6.0
	[Composition of Fixing Solution)	
15	Ammonium thiosulfate (50% aqueous solution)	162 ml
	Sodium sulfite, anhydrous	12.4 g
	Add water to make	l ltr.
	Adjust the pH value with acetic acid to	рн 6.5
	Each sample thus obtained through the ab	ove
20	processing was shielded against light and all	owed to
	stand at 77°C; in this way the cyan transmiss	ion
	density in the maximum density area were each	changed.
	The results thereof are shown in Table 1, bel	ow.

Table 1

			I	Light Shielded at 77°C	1ded at 7	J.C	
Sample		Devel- oper	Same	4 days	8 days	16 days	4
for)	(for Control)	3	1.5 7	1.50	1.4.1	1.28	
(The	C (The Invention)	€)	1.55	1.54	1.49	1.4.1	
		€)	1.58	1.64	1.72	1.70	
B (for	(for Control)	(E)	1.61	1.4 4	1.17	0.9%	
D (The	(The Invention)	(B)	1.58	1.48	1.29	1.09	
J	*	(£)	1.64	1.5 5	1.34	1.18	
(The	E (The Invention)	<u>(C</u>	0.03	0.2 7	0.42	0.4.0	
J		(Q)	0.03	0.18	0.3 5	0.29	

In the above Table, it can be seen that a heat-color-developable leuco dye was formed after the process was completed in each of Samples E and F which were processed with Developer (C) and that said leuco dye was gradually converted into the dye in an atmosphere at 77°C. It can be seen that every one of Samples C, E and D, F (of the invention) which were processed with Developers (A) and (B) respectively displayed a heat-fading prevention effect as compared with Control Samples A and B.

In addition the process of the invention can be combined with a well-known heat fading prevention process.

Example 2

Onto a paper support coated on both sides

15 thereof with polyethylene containing titanium oxide,
the undermentioned layers from 1st to 6th layer in
order from the support were coated. The components
and amounts thereof coated were as follows:

(Sample M)

lst Layer (Blue-sensitive emulsion layer)

	Yellow Coupler:	
	TOTION COMPTCE,	
5	α-(l-Benzyl-2,4-dioxoimidazolidine-3-yl)- α-pivalyl-2'-chloro-5'-[γ-(2,4-di-t- pentylphenoxy) butanamide] acetanilide	0.71g/m ²
	2,5-di-t-octylhydroquinone	20mg/m ²
	Dibutyl phthalate	$0.48g/m^2$
10	Silver chlorobromide (in silver equivalence)	0.38g/m ²
	Ossein gelatin	$1.8g/m^2$
	Gelatin hardener (Bis-vinylsulfonyl ethane)	27.0mg/m ²
	2nd Layer (Inter-layer)	
15	Tinuvin-328 (Brand name of Ciba-Geigy)	0.17g/m ²
	2,5-di-t-octylhydroquinone	$37mg/m^2$
	Tricresyl phosphate	$0.17g/m^2$
	Ossein gelatin	$0.7g/m^2$

3rd Layer (Green-sensitive emulsion layer)	
Magenta Coupler (1)	
<pre>3-{2-chloro-5-[1-(octadecyl) succinimide]anilino}-1-(2,4,6- trichlorophenyl)-5-pyrazolone</pre>	0.35g/m ²
Magenta Coupler (2)	
<pre>3-{2-chloro-5-(lauroylamide) benzamide}-1-(2,4,6-trichlorophenyl)- 4-acetamide-5-pyrazolone</pre>	0.10g/m ²
10 2,5-di-t-octylhydroquinone	10.0mg/m^2
Tricresyl phosphate	$0.17g/m^2$
Dioctyl phthalate	$0.26g/m^2$
Silver chlorobromide (in silver equivalent)	0.45g/m ²
15 Ossein gelatin	1.8 g $/$ m 2
<pre>Gelatin hardener (Bis- vinylsulfonylethane)</pre>	20mg/m ²
4th Layer (Interlayer)	
Tinuvin-328	$0.35g/m^2$
202,5-di-t-octylhydroquinone	50mg/m^2
Tricresyl phosphate	$0.35g/m^2$
Ossein gelatin	$1.0g/m^2$
5th Layer (Red-sensitive emulsion layer)	
CyanCoupler:	
252-[2-(2,4-di-t-pentylphenoxy) butanamide]-4,6-dichloro-5-methylphenol	0.35g/m ²
2,5-di-t-octylhydroquinone	8mg/m ²
2,6-di-t-butyl-4-(2,4-di-t-butylphenoxy-carbonyl)phenol	0.llg/m ²

	Dioctyl phthalate	$0.13g/m^2$
	Silver chlorobromide (in silver equivalent)	0.25g/m ²
	Ossein gelatin	1.4g/m ²
5	Gelatin hardener (Bis-vinylsulfonylethane)	20mg/m ²
	6th Layer (Protective layer)	
	Ossein gelatin	$0.85g/m^2$
	Pig-skin gelatin	$0.15g/m^2$
10	Phenol	4mg/m^2
	Gelatin hardener (Bis-vinylsulfonylethane)	30mg/m ²

Each of the above-mentioned layers contains a surface active agent, thickener, mordant, irradiation dye and the 15 like, besides the above components.

In addition to the samples, Sample N was prepared by omitting Magenta Coupler (2) from the components of the above-mentioned Sample M.

Samples M and N were exposed to light through a

20 step-wedge with 0.075 constant steps for 500 C.M.S., 1/2

sec, and the following processing steps with the following processing solutions were then made.

(Processing Steps)

	(1)	Color-developing Bath	35°C	3 min.
25	(2)	Bleach-Fix Bath	35°C ·	1.5 min.
	(3)	Washing	18 - 22°C	2 min.

(Color-developing Solution)

This is the same as Developer B of Example-1.

(Bleach-Fix Solution)

5	Ethylenediaminetetraacetic acid iron ammonium	62	g
	Ethylenediaminetetraacetic acid diammonium	6.5	g
	Ammonium thiosulfate	13.4	g
	Sodium sulfite, anhydrous	3	g
10	Add aqueous ammonia and water to adjust the pH value to	рН 7.0	
	and to make	1 1t	tr

Samples M and N thus prepared were exposed to xenon-arc light to measure the residue of the 15 magenta components. The residual rates (%) thereof in the region of 1.0 of the initial reflection density are shown in Table 2, below.

Table 2

		Xen	on-Arc Il	luminatio	n (J/m ²)	
2 0	Sample	0	5.0x10 ⁷	1.1x10 ⁸	1.9x10 ⁸	4.5x10 ⁸
	M - (Invention)	100	91	87	85	73
	N - (Control)	100	82	72	56	34

wherein ${\rm J/m}^2$ means Joule per square meter, the energy equivalent to a quantity of illumination.

As is obvious from the above Table 2, in contrast with the case of Sample N having only Magenta 5 Coupler (1), in the case of Sample M of the invention containing Magenta Coupler (2) capable of forming a light-color developable leuco dye, the magenta coupler thereof is prevented apparently from fading because in a color developing bath a magenta dye and 10 a leuco dye are simultaneously formed by Magenta Coupler (1) for the former and by Magenta Coupler (2) and 4-(N-ethyl-N- β -methylsulfonamide ethylamino)-2methyl aniline for the latter, and said leuco dye develops color gradually upon illumination by a 15 Xenon-Arc light. The effects of the process of this invention can be enhanced when a color-fading preventive (such as 1,4-dioctyloxy-2,5-di-t-pentyl benzene) is incorporated in the green-sensitive emulsion layer of Sample M.

CLAIMS

- 1. A process for reducing or preventing a dye image in a color image forming material, or a dye image in a colored print, from discoloring and/or fading which comprises forming a color-developable leuco dye which develops color under the action of heat and/or light either in said color image forming material, or upon exposure of said image forming material, or in said colored print.
- 2. A process according to claim 1 wherein said 10 leuco dye is formed from a developer having a sulfonamide group and a coupler.
 - 3. A process according to claim 2 in which the developer is one having the formula:

Au-Co-NH-SO2-Y

- 15 wherein Au represents an auxochrome, Co represents a group having at least one conjugated double bond and Y represents a group which imparts one or more physical properties to the developer.
- 4. A process according to claim 3 wherein Au represents -R, -OR or NRR' or a halogen atom wherein R and R' independently represent hydrogen or an unsubstituted or substituted alkyl group or, when Au represents -NRR', R and R', together with the nitrogen atom to which they are attached, form a nitrogen-containing
- 25 saturated hetero ring, Co represents a butadienylene, phenylene or substituted phenylene group and Y represents a hydroxyl group or a salt thereof, an alkyl group, an amino group or an aryl group.

- 5. A process according to any one of the preceding claims wherein the image forming material is a photosensitive silver halide emulsion material.
- 6. A process according to claim 5 wherein the 5 leuco dye is formed during processing of the material following imagewise exposure.
 - 7. A process according to claim 5 or 6 wherein the material also comprises a cross oxidizer.
- 8. A color image forming material which
 10 comprises color image forming ingredients characterised
 by also comprising a color-developable leuco dye, or the
 precursors therefor, which develops color under the
 action of heat and/or light.
- 9. A colored print which comprises a color 15 developable leuco dye, or the precursors therefor, which develops color under the action of heat and/or light.



EUROPEAN SEARCH REPORT

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Category		indication, where appropriate, int passages	Relevant to claim		ATION OF THE ON (Int. Cl. 3)
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	Place of search	Date of completion of the search		Examine	er
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CATEGORY OF CITED DOCUMENTS

- X: particularly relevant if taken alone
 Y: particularly relevant if combined with another document of the same category
- technological background O: non-written disclosure
 P: intermediate document

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- T: theory or principle underlying the invention E: earlier patent document, but published on, or
- after the filing date

 D: document cited in the application
 L: document cited for other reasons
- &: member of the same patent family, corresponding document