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3,736,136

DYE DIFFUSION TRANSFER PROCESS FOR THE PRODUCTION OF POSITIVE COLOR PHOTOGRAPHIC IMAGES

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12 Claims

ABSTRACT OF THE DISCLOSURE

Positive color photographic images are produced by a modified dye diffusion transfer process including exposure of a silver halide emulsion layer transfer of a diffusing development inhibiting substance from the exposed areas to an unexposed developable emulsion layer whereby development is inhibited by the said transferred development inhibiting substance and transfer of a dye from the said second emulsion layer which is split off from a non-diffusing dye-giving compound upon development, to an image-receiving element, whereby the non-diffusing dye-giving compound has the formula defined below.

The invention relates to a process for the production of positive color photographic images by the dye diffusion transfer process, and to a material for carrying out the process.

The production of positive colored images by the dye diffusion transfer process is already known. In one known process, for example, so-called dye-developers are used, i.e. compounds which contain in the same molecule both a dye radical and a group capable of developing silver halide. When light-sensitive silver halide emulsion layers which have been exposed imagewise and thus immobilized in the layer whereas the remaining dye-developer which has not been oxidized remains capable of diffusion and is transferred to an image-receiving layer where it forms the positive image. This process has been described, for example, in German patent specification No. 1,196,075. Very complicated materials are, however, required for carrying out this process. Furthermore, owing to the nature of the groups which render the compound hydrophilic and capable of diffusion (generally phenolic hydroxyl groups), it is necessary to operate at very high pH values.

In another process, which has been described, for example, in German patent specification Nos. 1,147,843 and 1,199,129, non-diffusing color couplers are used from which dyes which are capable of diffusion are split off in the process of color development and these dyes are transferred to the image-receiving element. In order to obtain positive images by this process, which is basically a negative process, light-sensitive dye-giving elements are used which consist of at least one layer combination of a light-sensitive silver halide emulsion layer and another unexposed developable emulsion layer which contains the said non-diffusing color coupler. The light-sensitive silver halide emulsion layer is developed with color developers

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in the presence of so-called DIR couplers, i.e. in the presence of couplers which, when reacted with oxidized colour developers, split off substances which inhibit development (DIR=development inhibitor releasing). The development inhibiting substances which are liberated imagewise in the light-sensitive layer diffuse into the adjacent unexposed developable emulsion layer where they inhibit development imagewise. The uninhibited (positive) portions of the unexposed developable emulsion layer are developed by the remaining developer whose oxidation products then react with the non-diffusing couplers to form diffusible dyes which are transferred imagewise to the image-receiving element. According to German patent specification No. 1,229,389 suitably substituted non-diffusing hydroquinone compounds which by reaction with the developer oxidation products are oxidized to the corresponding quinones, thereby splitting off development inhibiting mercaptans, can be used in such a process instead of the DIR couplers.

The non-diffusing couplers used in the last mentioned processes are compounds in which a bond is split by the reaction with oxidized color developers in the course of development, which bond links the non-diffusing coupler radical via an intermediate member to a diffusible dye radical or second coupler radical or it links a radical which renders the compound non-diffusing to a coupler radical which is in itself capable of diffusion. The usual types of known photographic couplers have been described for this purpose, e.g. pyrazolinone-(5) derivatives, phenol derivatives and α -naphthol derivatives and open chain ketomethylene compounds. The "coupling position" of the coupler molecule is understood to mean the carbon atom in the 4-position in the case of pyrazolinone-(5) compounds, in the case of phenol and α -naphthols it is also understood to be the carbon atom in the 4-position and in the case of open chain ketomethylene couplers it is understood to be the carbon atom of the methylene group in the group $\text{CO}-\text{CH}_2-\text{CO}$.

In the process of coupling with oxidized color developers, the substituent in the coupling position is split off and there results, depending on the method used for carrying out the process, either a diffusing azomethine dye or, if the coupler portion is non-diffusing, a diffusing dye which may be of some other type. The resulting diffusible dyes are transferred from the light-sensitive element to an image-receiving element which is in close contact with it.

These last mentioned processes have several disadvantages. For example, the diffusing dyes are generally azomethine dyes and accordingly are only moderately stable and fast to light. In cases, however, where the substances split off in this process from the coupling position of the non-diffusing couplers are diffusing dyes which may belong to some other class of dyes and may therefore be more fast to light, other serious disadvantages arise.

That part of the molecule which is split off in the process of oxidative coupling is linked to the "coupling position" via a "cleavable bond," i.e. a bond which can be split off. The following are examples of such cleavable bonds: azo ($-\text{N}=\text{N}-$), oxy ($-\text{O}-$), mercury ($-\text{Hg}-$), alkylidene (includes both $>\text{CH}-$ and $=\text{CH}-$), thio ($-\text{S}-$) or dithio ($-\text{S}-\text{S}-$).

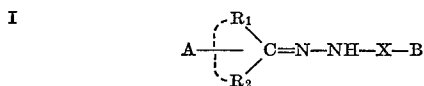
The proposed groups are not all found to be equally advantageous. Some of them, e.g. the groups $-\text{O}-$,

—Hg— and =CH—, are unsuitable in practice because splitting off these groups takes place too slowly. Moreover, in the patents relating to these processes, e.g. in German Pat. Nos. 1,147,843 and 1,199,129, the only bond which has been specifically disclosed as the cleavable bond between the light-fast dye portion and the non-diffusing coupler portion is the azo bond. If, however, the azo group is chosen as bridge member, reaction with the oxidized color developer results, as is well known, in the formation of nitrogen which partly escapes from the layer in the form of small bubbles and interferes with the necessary contact between the dye-giving element and the image-receiving element. This is particularly the case when elevated temperatures are employed to accelerate the process.

However, if the thioether group which is also very easily split off from the coupling position of couplers in the reaction with oxidized color developers, is used in this dye diffusion process as bridge member between the diffusion-fast portion of coupler and the diffusible dye portion, this entails disadvantages since, as is well known, the mercaptans formed in this reaction react very readily with silver halide, either chemically to form silver mercaptans or by absorption at the silver halide. This fact is made use of, for example, when using DIR couplers. These characteristics, however, stand against the requirement of rapid, and as far as possible quantitative, diffusion of the liberated dyes.

It is an object of the present invention to provide an improved process for the production of positive colored images by the dye diffusion transfer process, and to provide a suitable photographic material for this process.

This invention therefore relates to a dye diffusion transfer process for the production of positive photographic images in which a dye-giving light-sensitive element consisting of at least one combination of a light-sensitive silver halide emulsion layer and, in combination with this layer, a non-diffusing compound (DIR compound) which splits off a diffusing, development inhibiting substance in the reaction with oxidation products of the color developer, and an unexposed developable emulsion layer which contains a non-diffusing dye-giving compound, is exposed imagewise and developed with a color developer, and in which the development inhibiting substance is split off imagewise from the DIR compound by the color development in the areas corresponding to the silver image (negative) formed in the light-sensitive silver halide emulsion layer, the said development inhibiting substance which has been split off diffusing into the unexposed developable emulsion layer where it inhibits development in areas corresponding to the image, whereupon, as the uninhibited portions of the unexposed developable emulsion layer (positive) are being developed, diffusion dyes are liberated from the non-diffusing dye-giving compound by the oxidation products of the color developer and transferred to an image-receiving element. The process is characterized in that the unexposed developable emulsion layer contains a non-diffusing dye-giving compound having the following Formula I:



wherein

R₁ represents hydrogen, an alkyl group with up to 20 carbon atoms and preferably with 1 to 5 carbon atoms, an aralkyl group, e.g. benzyl, an aryl group, e.g. phenyl, or an amino group which is substituted with alkyl or aryl, for example with phenyl, and in which two alkyl groups on the nitrogen atom may be joined to form a ring.

R₂ represents an alkyl group with up to 20 carbon atoms, an aralkyl group, e.g. benzyl, an aryl group, e.g. phenyl, an acyl group which is derived from aliphatic carboxylic acids with up to 20 carbon atoms or from aromatic carboxylic acids such as benzoyl, or an amino group which is substituted with alkyl or aryl, for example with phenyl, and in which two alkyl groups on the nitrogen may be joined to form a ring, or

R₁ and R₂ taken together represent the ring members required to complete an isocyclic or heterocyclic group, preferably 5-membered or 6-membered, which may have a condensed benzene ring; at least one of the radicals R₁ and R₂ carries the group A;

X represents a sulfonyl group, a carbonyl group or a single chemical bond;

A represents a photographically inert radical rendering the dye-giving compound resistant to diffusion; and B represents a dye radical; or

A represents a dye radical either alone or together with R₂; and

B represents a photographically inert radical rendering the dye-giving compound resistant to diffusion.

Radicals which render the compound resistant to diffusion are understood to be radicals which enable the compounds according to the invention to be incorporated in a diffusion-fast form in the hydrophilic colloids customarily used in photographic materials; these radicals must, of course, in no way influence the photographic properties of the layers. The radicals preferably used for this purpose are organic radicals which in general may contain straight chain or branched chain aliphatic groups and, if desired, also isocyclic or heterocyclic aromatic groups. The aliphatic portion of these radicals generally contains from 8 to 20 carbon atoms. These radicals are connected to the remaining part of the molecule either directly or indirectly, e.g. by way of one of the following groups: —CONH—, —SO₂NH—, —CO—, —SO₂—, —NR— in which R represents a hydrogen atom or an alkyl group, or —O— or —S—. The radical which renders the compound resistant to diffusion may also contain groups which render the compound water-soluble, e.g. sulfo groups or carboxyl groups; these groups may also be present in the anionic form. Since the diffusion characteristics depend on the molecular size of the whole compound, short chain radicals may in some cases be used as the ballasting radicals which render the compound resistant to diffusion, e.g. if the molecule as a whole is large enough.

The dye radicals may in principle be the dye radicals of any class of dye, provided they are sufficiently diffusible after they have been split off to be able to diffuse in to the image-receiving layer through the layers of the light-sensitive material. On account of this requirement, the dye radicals preferably have at least one but generally several groups which render them water-soluble. Suitable groups which render them water-soluble are inter alia carboxyl groups, sulfo groups, hydroxyl groups or hydroxyalkyl groups. The following are given as examples of dyes which are particularly suitable for the process of the invention: azo dyes, anthraquinone dyes, phthalocyanine dyes, indigoid dyes and triphenylmethane dyes.

One of the features in which the process according to the invention differs from the processes mentioned above is that compounds which contain none of the coupler radicals normally used in conventional color photography are used for the process of the invention. Another difference between this process and the known processes lies in the larger choice of developer substances which may be used, which is due to the fact that the color shade of the transferred dyes does not depend on the developer.

The dyes which are split off from the dye-giving substances according to the invention by the reaction with the oxidation products of the developer must be sufficiently hydrophilic to ensure rapid, and as far as possible,

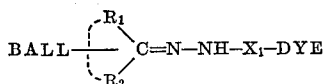
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quantitative diffusion. The hydrophilic character is generally imparted by sulfo groups or carboxyl groups. It is known from the chemistry of couplers that a suitable balance must be achieved between the size of the radicals which render the compound resistant to diffusion and the number of groups which render the compound soluble in order to achieve both sufficient resistance to diffusion and sufficient solubility in aqueous alkaline media; the resistance to diffusion decreases with an increasing number of solubilizing groups. The larger the radical which renders the compound resistant to diffusion, the larger the number of solubilizing groups required for diffusion.

Two conditions must be fulfilled in the dye diffusion process according to the invention. The dye-giving compounds according to the invention must be incorporated in a completely diffusion resistant form in the unexposed developable layer of the light-sensitive element, and the dyes liberated by the reaction with the oxidation products of the developer must be readily soluble in the reaction media and capable of diffusion through them. The dye portion of the molecule is generally very large and therefore the dye which is split off must be very hydrophilic in order that the necessary rate of diffusion may be achieved, i.e. it should contain a large number of solubilizing groups. On the other hand, the compounds used according to the invention must satisfy the same requirements as regards resistances to diffusion as is necessary in the known chromogenic processes, i.e. these compounds should contain as few solubilizing groups as possible in order to achieve optimum resistance to diffusion. It is, therefore, desirable that solubilizing groups are formed in the splitting reaction which remain with the dye portion of the molecule and impart to it a certain additional capacity for diffusion.

According to a particularly advantageous embodiment of the process of the invention, therefore, compounds of the following Formula II incorporated in a diffusion-fast form are used:

(II)



wherein

R₁ and R₂ having the meanings given above, and at least one of the radicals R₁ and R₂ carries the group D; X₁ represents a sulfonyl group or a carbonyl group; BALL is a ballasting photographic inert radical rendering the dye-giving compound resistant to diffusion; and DYE is a dye radical.

In this embodiment, both the dye radical and the radical rendering the compound resistant to diffusion may contain solubilizing groups, preferably sulfo groups. In this way, it is possible to adapt the diffusion resistance of the dye-giving compound and the diffusibility of the dyes and their capacity to be absorbed by the mordants of the receiving layer to the practical requirements in any given case by suitable choice of the number and position of the solubilizing groups. It is found to be a particular advantage of this embodiment of the process, e.g. when X₁ denotes a sulfonyl group, that one may use dye-giving compounds which do not contain any solubilizing groups or fewer than required for diffusion. Extremely high resistance to diffusion is thereby obtained. The dye which is split off is nevertheless capable of diffusing because when it is split off by the oxidation product of the developer, an additional group which renders it water-soluble is formed from the sulfonyl group, and this solubilizing group remains with the dye portion of the molecule. Good diffusibility of the dye which has been split

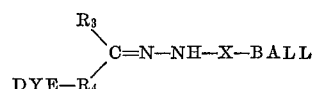
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off is therefore achieved together with extreme insolubility and hence resistance to diffusion of the dye-giving compounds in the layer of the light-sensitive element.

In this embodiment of the process, preferably R₁ and R₂ taken together denote the ring members required to complete a heterocyclic group comprising a 5-membered or 6-membered heterocyclic ring. Suitable heterocyclic groups are, for example, the oxazoline, benzoxazoline, thiazoline, benzothiazoline, imidazoline, benzimidazoline, pyrrolidine, indolenine, isoindolenine, 1,2 - dihydropyridine, 1,4 - dihydropyridine, dihydroquinoline, 1,2 - dihydroquinazoline, thiadiazoline, pyrazoline or triazoline group. The heterocyclic group preferably carries at least one polar group which renders it water-soluble, for example a sulfo or carboxyl group, either directly or via a substituent, e.g. a short chain alkyl group. Other combinations are also suitable, e.g. R₁=H, and R₂=aryl. Fb preferably denotes a light-fast dye radical, e.g. an azo dye radical or an anthraquinone dye radical.

According to another embodiment of the process of the invention, a compound of the following Formula III incorporated in a diffusion-fast form is used:

(III)



wherein

R₃ represents a hydrogen atom, an alkyl group preferably containing 1 to 5 carbon atoms, e.g. methyl, ethyl or propyl, an aralkyl group, e.g. benzyl, or an aryl group, e.g. phenyl;

R₄ represents an aryl group, e.g. a phenyl group, which may be part of the chromophoric system of the dye radical;

X represents a sulfonyl group, a carbonyl group or a single chemical bond;

BALL represents a ballasting photographic inert radical rendering the dye-giving compound resistant to diffusion; and

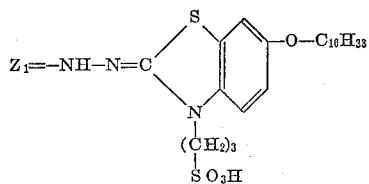
DYE represents a dye radical, either alone or together with R₄.

In this case, R₄ is preferably an aryl group, e.g. phenyl, to which a dye radical is linked either directly or indirectly, or which itself constitutes part of the chromophoric system of such a dye radical. In the latter case, the aryl group may be linked in any position, for example the phenyl group in the o-, m- or p-position, via an azo group to an isocyclic or heterocyclic aromatic group, e.g. to an aryl group, or to a pyrazolone-(5) group, thus forming an azo dye with this group.

The dye-giving compounds which are originally incorporated in a diffusion-fast form in the layer are split by the reaction with the oxidation products of the developer so that the dyes are released from their bond. Since they generally contain one or even more solubilizing groups, they are capable of diffusing into the image-receiving layer where they are fixed by the mordant. The radical which renders the compound resistant to diffusion remains behind in the emulsion layer of the light-sensitive element.

Since no new dye is formed in any of the embodiments of the process and no dye is destroyed as, for example, in the azo dye bleaching process, it is a characteristic of the diffusion transfer process of the invention that after transfer of the dye, the two layers, i.e. the emulsion layer and the image-receiving layer, have the same color but in the opposite gradation.

The following are examples of suitable dye-giving compounds:



		Color of the transferred dye
A.....		Blue-green.
B.....		Do.
C.....		Do.
D.....		Do.
E.....		Yellow.
F.....		Do.
G.....		Do.
H.....		Do.

Color of the
transferred dye

I.....		
K.....		Yellow.
L.....		Do.
M.....		Magenta.
N.....		Do.
O.....		Do.
P.....		Do.
Q.....		Do.

The color photographic material which is suitable for carrying out the process of the invention contains a light-sensitive dye-giving element which comprises at least one combination of a light-sensitive silver halide emulsion

layer and an unexposed developable emulsion layer which contains a non-diffusing, dye-giving compound of the general Formula I, II or III.

The light-sensitive dye-giving element preferably com-

prises three such combinations of layers which may be separated from each other by interlayers but in which each light-sensitive silver halide emulsion layer is sensitive to a different region of the visible spectrum. For example, the light-sensitive element may contain a red-sensitive, a green-sensitive and a blue-sensitive silver halide emulsion layer. The dye-giving compounds which are incorporated in a diffusion-fast form in the unexposed developable emulsion layers are preferably chosen so that the color of the dyes which are split off by the reaction with the oxidation products of the developer is complementary to the sensitivity or sensitization of the associated adjacent silver halide emulsion layer.

In combination with the light-sensitive silver halide emulsion layers, the light-sensitive element contains non-diffusing compounds which in their reaction with the oxidation products of color developers split off a diffusing substance which inhibits development. These last mentioned compounds may, for example, be so-called DIR couplers, i.e. compounds which react with oxidation products of a color developer to yield a dye and a development inhibiting substance, for example a mercaptan. DIR couplers of this type have been described in German Offenlegungsschrift No. 1,422,839. They may be represented by the following formula:



wherein

Cp represents a color coupler radical, and R represents an organic radical which is split off together with the sulfur atom of the thioether bridge in the reaction with the oxidation products of the color developer and thus forms a diffusing mercapto compound which has a development inhibiting effect.

Another important group of compounds which react with oxidation products of color developers to split off development inhibiting substances and which are preferred for the process of the invention have been described in U.S. Pat. No. 3,632,345. These compounds are not color couplers and will therefore be termed "DIR-compounds" hereinafter to distinguish them from the DIR couplers mentioned above. They are represented by the following formula:



wherein

E represents a group which is split off together with the sulfur atom of the thioether bridge in the reaction with the oxidation products of the color developer to form a mercapto compound which has a development inhibiting action, e.g. to form heterocyclic mercapto compounds such as mercaptotetrazoles, especially 1-phenyl-5-mercapto-tetrazole, 1-nitrophenyl-5-mercaptotetrazole or 1-naphthyl-5-mercaptotetrazole; mercaptothiazoles such as mercaptobenzothiazoles or mercaptonaphthiazoles, mercaptooxadiazoles, mercaptopyrimidines, mercaptothiadiazoles such as 2-mercaptothiadiazole triazines; mercaptotriazines, mercaptotriazoles; mercapto-substituted benzenes such as thiophenol; or derivatives of thioglycolic acid, cysteine or glutathione;

R=(1) a hydrogen atom;

(2) an alkyl group preferably containing up to 18 carbon atoms;

(3) an aralkyl group such as benzyl or phenyl ethyl;

(4) a cycloalkyl group such as cyclohexyl;

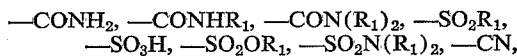
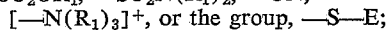
(5) an aryl group, especially aryl radicals of the phenyl or naphthyl series;

(6) a heterocyclic radical having 5 to 6 ring members, which rings may contain one or more hetero atoms such as N, O, S or Se and condensed benzene or

naphthalene rings, e.g. benzoxazole, benzothiazole and the like, or

(7) the group $-\text{S}-\text{E}$;

X=one of the following groups which activate the carbon atom to which X, R and $-\text{S}-\text{E}$ are attached:



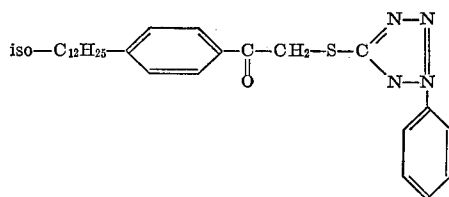
R_1 =(1) a saturated or olefinically aliphatic radical containing up to 18 carbon atoms, preferably up to 5 carbon atoms, which radicals may be substituted, e.g. with hydroxyl, alkoxy, halogen or aryl radicals, especially phenyl;

(2) an aryl group, preferably phenyl or naphthyl, the phenyl rings being substituted, if desired; or

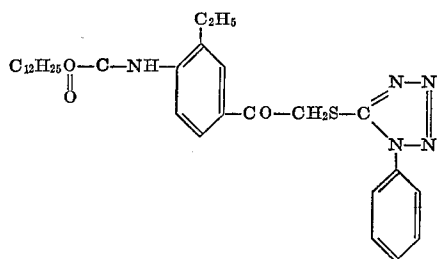
(3) a 5-membered or 6-membered heterocyclic radical which may contain one or more hetero atoms such as N, O, S or Se and condensed benzene or naphthalene rings; two of the substituents R_1 , for example in the quaternary amino groups or sulfonamido groups shown above, may together represent the ring members required to complete a saturated 5-membered or 6-membered ring which contains nitrogen, e.g. piperidine, pyrrolidone or morpholine.

The following DIR compounds have been found to be especially suitable:

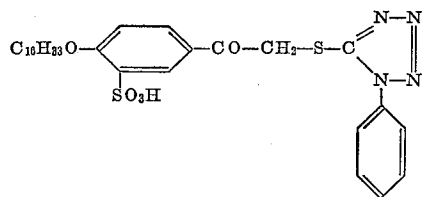
(1)



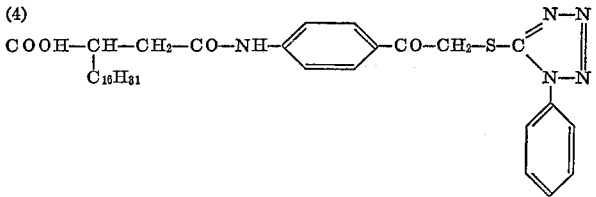
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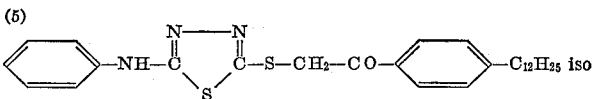
(3)



(4)



(5)



In the light-sensitive element, the DIR couplers and the DIR compounds described above are closely associated with the light-sensitive silver halide layers, i.e.

they are situated as close as possible to the position where the oxidation products of the color developer are formed. They may, therefore, be directly contained in the light-sensitive silver halide emulsion layers. The development inhibiting substances produced on reaction with the DIR couplers or ID compounds with oxidation products of color developers should, however, produce their action mainly in the unexposed developable emulsion layer and not in the light-sensitive silver halide emulsion layers. It has, therefore, in many cases been found advantageous not to incorporate the DIR couplers or the DIR compounds in the silver halide emulsion layer but in a layer of binder arranged between the silver halide emulsion layer and the unexposed developable emulsion layer.

The silver halide emulsions used in the light-sensitive layers of the light-sensitive, dye-giving element are ordinary highly sensitive photographic silver halide emulsions, which form negative silver images and which contain silver chloride, silver bromide or mixtures thereof, if desired with a small silver iodide content of up to 10 mols percent. The binder used for the silver halide may be gelatin or some other hydrophilic colloid known for photographic purposes; gelatin is preferred.

The said light-sensitive silver halide emulsions may or may not be sensitized. They may, for example, contain spectral sensitizers, e.g. the usual monomethine or polymethine dyes such as cyanines and preferably those which have sulfobetaine groups, hemicyanines, streptocyanines, merocyanines, oxonoles, hemioxonoles, styryl dyes or the like or methine dyes which have three or more nuclei, for example rhodacyanines or neocyanines. Sensitizers of this type have been described in the work by F. M. Hamer "The Cyanine Dyes and Related Compounds" (1964).

The light-sensitive emulsions may also contain other additives generally used in such products, e.g. chemical sensitizers, antifogging agents, coating agents, gelatin hardeners or plasticizers.

The unexposed, developable emulsion layers which are adjacent to the light-sensitive silver halide emulsion layers contain metal salts which are capable of being reduced and which may be reduced by the developer substances in the presence of development nuclei and the development of which may be inhibited by the development inhibiting substances already mentioned. These compounds are preferably silver salts of organic and inorganic acids, such as silver halides, e.g. silver chloride, silver bromide or mixtures of these salts, silver citrate, silver oxalate, silver phosphate, silver thiosulfate, silver cyanide or silver thiocyanate. Palladium bromide, palladium cyanide or copper-(II) bromide are also suitable. Metal salts of this type may be developed without exposure in the presence of development nuclei, e.g. in the presence of colloidal noble metals such as silver or gold or colloidal metal sulfides, metal selenides or metal tellurides, e.g. lead sulfide, nickel sulfide, cadmium sulfide, silver sulfide, silver selenide, silver telluride, copper sulfide, zinc sulfide and mercury sulfide. Sodium hydrosulfide, colloidal sulfur and organic sulfur compounds such as thiourea or xanthates are also suitable physical development nuclei for the above mentioned metal salts. Another possibility of rendering the metal salt emulsions developable without exposure consists in treating them with chemical reducing agents such as certain boron hydride compounds, or in exposing them to light, which causes the emulsions to become fogged.

Interlayers are arranged in the material according to the invention between the individual layer combinations which consist of one light-sensitive silver halide emulsion layer, one unexposed developable emulsion layer and, if desired, a layer of binder which can contain the DIR couplers or DIR compounds, these interlayers serving to ensure that the action of the development inhibiting substances which are liberated by the reaction with the oxidation products of the color developer is restricted to the given layer combination. These separating interlayers may advantageously contain a small amount silver halides

such as silver chloride, silver bromide, silver iodide or mixtures of these salts which are capable of forming insoluble salts with mercaptans. Other compounds which react with mercaptans are, for example, colloidal metals or colloidal metal sulfides, selenides or tellurides. If these separating layers contain light-sensitive silver salts, they should be less sensitive to light than the light-sensitive silver halide emulsions of the dye-giving layer combinations.

The light-sensitive element of the color photographic material according to the invention may, therefore, have the following structure, for example:

a blue-sensitive silver halide emulsion layer and, associated with this layer, a non-diffusing compound which splits off a development inhibiting substance in the reaction with the oxidized color developer;

an unexposed developable emulsion layer containing a nondiffusing compound having one of the Formulae I, II and III, which splits off a diffusing yellow dye in the reaction with the oxidation products of the developer;

a separating layer;

a green-sensitized silver halide emulsion layer and, associated with this layer, a non-diffusing compound which splits off a development inhibiting substance in the reaction with oxidation products of the color developer;

an unexposed developable emulsion layer containing a non-diffusing compound having one of the Formulae I, II and III which splits off a diffusing magenta dye in the reaction with oxidation products of the developer;

a separating layer;

a red-sensitized silver halide emulsion layer and, associated with this layer, a non-diffusing compound which splits off a diffusing development inhibiting substance in the reaction with oxidation products of the color developer;

an unexposed developable emulsion layer containing a non-diffusing compound having one of the Formulae I, II and III which splits off a diffusing cyan dye in the reaction with oxidation products of the developer.

Individual layers or layer combinations in the light-sensitive element described above may, of course, be interchanged but in such a case care should be taken to ensure that the original association between sensitization and color of the dye split off on development is preserved.

According to one particular embodiment of this invention, the light-sensitive dye-giving element may be arranged on a conventional transparent or opaque support. In this case, the imagewise exposed material is processed by treating the light-sensitive element with an aqueous alkaline processing composition in the presence of a color developer substance, so that development of the light-sensitive silver halide, diffusion of the uninhibited portions of the unexposed developable emulsion and diffusion of the dyes which have been split off are initiated. The light-sensitive element treated in this way is brought into contact with a conventional image-receiving element which consists mainly of an image-receiving layer on a support. The dyes, which are now imagewise diffusible, are transferred to the image-receiving element where they produce the final image. When transfer has been effected, the light-sensitive element is separated from the image-receiving element.

The image-receiving element consists mainly of supporting a layer of binder which contains dye mordants for fixing the diffused acid dyes.

The mordants used for acid dyes are preferably long chain quaternary ammonium or phosphonium compounds or ternary sulfonium compounds, e.g. those described in U.S. patent specification Nos. 3,271,147 and 3,271,148. Certain metal salts and their hydroxides which form sparingly soluble compounds with the acid dyes may also be used. These dye mordants are dispersed in one of the usual hydrophilic binders in the receiving layer, e.g. in

gelatin, polyvinyl pyrrolidone, completely or partially hydrolysed cellulose esters or the like. Certain binders may, of course, function as mordants, e.g. copolymers or polymer mixtures of vinyl alcohol and N-vinyl pyrrolidone, e.g. those described in German Auslegeschrift No. 1,130,284, or those which are polymers of quaternary bases which contain nitrogen, e.g. polymers of N-methyl-2-vinyl pyridine as described, for example, in U.S. patent specification No. 2,484,430. Other suitable binders which function as mordants are, for example, guanil hydrazone derivatives of alkylvinyl ketone polymers as described e.g. in U.S. patent specification No. 2,882,156, or guanil hydrazone derivatives of acyl styrene polymers as described e.g. in German patent specification P 20 09 498. Other binders, e.g. gelatin, however, generally are added to the last mentioned mordanting binders.

According to another embodiment of the process, both elements may be arranged on the same layer directly, above one another. In that case, the layer directly mounted on the layer support is the image-receiving layer which contains a dye mordant in a binder, and the various layers of light-sensitive element are arranged above this. After exposure and development and when the dyes which have been liberated imagewise by development have diffused into the lowermost image-receiving layer, the light sensitive layers are washed. Readily soluble emulsions are generally used in that case, for example those based on polyvinyl alcohol or on cellulose ether phthalate which is soluble in alkalis.

According to a third embodiment of the process, a material comprising a transparent image-receiving layer on a transparent support and the light-sensitive element arranged over the image-receiving layer is used. The material is sealed off at the top by a covering layer which is impermeable to light, and thus forms a dimensionally stable unit which cannot be separated. After exposure, which is carried out through the transparent support, an aqueous alkaline processing composition which contains a pigment, preferably a white pigment, is pressed into the material between the light-sensitive element and the image-receiving element. This pigment-containing processing composition pressed into the material forms an intermediate layer which is impermeable to light but permeable to diffusing dyes. The dyes which have been split off in the process of development diffuse through the light-impermeable pigment layer into the image-receiving element where they form a colored reproduction of the original object. This reproduction is visible through the transparent support but with the sides reversed.

According to a fourth and particularly preferred embodiment of the process, the material used is very similar to that described above but it differs from it in that the layer which is impermeable to light but permeable to alkali and to diffusing dyes is arranged *a priori* between the light-sensitive element and the image-receiving element, and in that the light-impermeable covering layer mentioned above is not present during the exposure. In this case, exposure is carried out from the side remote from the transparent support. The light-sensitive element is then treated with an aqueous alkaline processing composition by applying the composition to the surface of the element or by dipping the element into it or wetting it with the composition, and the light-sensitive element and the covering layer which is impermeable to light are then pressed together. On development, dyes are split off in the light-sensitive element in an amount depending on the imagewise exposure which has taken place, and they diffuse through the intermediate layer which is impermeable to light into the image-receiving element where they form a colored reproduction of the original object which has been photographed. This colored copy is again visible through the transparent support but in this case without the sides being reversed. Apart from the fact that the sides are not reversed, this embodiment of the process has the advantage over the previous one that exposure

is not carried out through a transparent layer and other additional transparent layers and that the dyes which are split off on development are not required to pass through a layer of developer in their transfer to the image-receiving element. Both these factors have an advantageous effect on the sharpness of the images obtained.

Any of the colour developers customarily used in conventional color photography are suitable for development in this process, e.g. the usual aromatic compounds of the p-phenylene diamine type which contain at least one primary amino group. Suitable color developers are, for example,

N,N-dimethyl-p-phenylene diamine,
N,N-diethyl-p-phenylene diamine,
monomethyl-p-phenylene diamine,
2-amino-5-diethylamino toluene,
n-butyl-N- ω -sulfobutyl-p-phenylene diamine,
2-amino-5-(N-ethyl-N- β -methanesulfonamidoethyl-amino)-toluene,
N-ethyl-N- β -hydroxyethyl-p-phenylene diamine,
N,N-bis-(β -hydroxyethyl)-p-phenylene diamine, or
2-amino-5-(N-ethyl-N- β -hydroxyethylamino)-toluene.

Other suitable color developers have been described e.g. in J. Am. Chem. Soc. 73, 3100 (1951).

In one special embodiment of the process of the invention, color developers which are resistant to diffusion may also be used, for example those described in U.S. patent application Ser. No. 43,939; filed June 5, 1970. The diffusion-fast color developers are preferably used in a light-sensitive silver halide emulsion layer which also contains the DIR couplers or DIR compounds. Although a developer substance is also required to be present in the unexposed developable layers in the development process, this substance need not necessarily be a color developer since the dye-giving compounds of Formulae I, II and III also react with oxidation products of black-and-white developers to split off the diffusing dyes. For example, the unexposed developable emulsion layer may contain such a black-and-white developer in a diffusion-fast form, e.g. a diffusion-fast pyrocatechol derivative. A light-sensitive element of this kind which contains a diffusion-fast color developer and a diffusion-fast DIR compound in the light-sensitive silver halide emulsion layer and a diffusion fast black-and-white developer in the unexposed developable emulsion layer may be processed with an alkaline liquid or viscous activator compositions which preferably also contains phenidone or phenidone derivatives. On the other hand, an additional developer substance for developing the unexposed developable layer may also be added to the alkaline activator composition. On processing, this developer substance penetrates the layers and develops those portions of the unexposed, developable emulsion layer which have not been inhibited in their development by the development inhibiting substances.

The invention will now be explained with the aid of examples.

EXAMPLE 1

The following layers are applied to a transparent polyethylene terephthalate support:

- (1) A silver chloride emulsion containing per kg. 12 g. of silver and 24 g. of dye-giving compound D; silver application 0.8 g./m.². This layer is exposed to daylight for 20 seconds.
- (2) A 5% aqueous gelatine solution containing per kg. 12 g. of DIR compound No. 4. This compound is applied in an amount of 0.6 g./m.².
- (3) A red-sensitized silver iodobromide emulsion containing per kg. 35 g. of silver, 4 mols percent of which is in the form of silver iodide. The silver application is 1.3 g./m.².

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After exposure through a step wedge, the material is dipped in a developer of the following composition for 30 seconds together with an image-receiving layer:

12 g. of N-ethyl-N-β-hydroxyethyl-4-amino aniline,
25 g. of potassium carbonate
0.5 g. of KBr,
0.3 g. of anhydrous sodium sulfite,
0.8 g. of ascorbic acid,
water up to 1000 ml.

The image-receiving layer consists of a pigmented cellulose acetate support on which a 5% aqueous gelatine solution containing per kg. 30 g. of octadecyl-trimethyl-ammonium bromide has been applied. Amount of mordant applied: 3 g./m.².

The negative and the image-receiving layer are then pressed together for 3 minutes. After separation of the layers, a positive cyan color wedge having a density maximum of 1.2 and a density minimum of 0.25 is obtained.

EXAMPLE 2

The following layers are applied to a transparent cellulose triacetate support:

- (1) A silver chloride emulsion containing per kg. 12 g. of silver, 20 g. of the dye-giving compound N and 10 ml. of a 2% aqueous suspension of colloidal silver sulfide; silver application 0.8 g./m.².
- (2) A green-sensitized silver iodobromide emulsion containing per kg. 17.3 g. of silver of which 4 mols percent is silver iodide, and 20 g. of DIR compound No. 3; silver application 1.3 g./m.².

After exposure through a step wedge, the material is dipped in a developer of the following composition for 30 seconds together with an image-receiving layer as in Example 1:

10 g. of N-ethyl-N-β-hydroxyethyl aniline,
0.2 g. of ascorbic acid,
20 g. of potassium carbonate,
0.5 g. of anhydrous sodium sulfite,
0.3 g. of sodium thiosulfate,
water up to 1000 ml.;
pH adjusted to 11.5.

The material and the image-receiving layer are pressed together for 3 minutes. After separation of the layer, a positive purple color wedge is obtained.

EXAMPLE 3

The following layers were applied to a transparent support:

- (1) A 5% aqueous solution of a copolymer of 2 parts by weight of methyl vinyl ether and 3 parts by weight of maleic acid (molecular weight approximately 50,000); thickness of the layer 4μ;
- (2) a 2% aqueous polyvinyl alcohol solution; thickness of the layer 3μ;
- (3) a 5% aqueous gelatin solution containing 30 g. of octadecyl-trimethyl-ammonium sulfate per litre; thickness of the layer 5μ;
- (4) a 5% aqueous gelatin solution containing 1000 g. of TiO₂ per litre; thickness of the layer 3μ;
- (5) a 5% aqueous gelatin solution containing 60 g. of carbon black per litre; thickness of the layer 1μ;
- (6) a silver chloride emulsion containing per kg. 15 g. of the dye-giving compound D and 10 ml. of a 2% suspension of colloidal silver sulfide; silver application 0.4 g./m.²;
- (7) a red-sensitized silver iodobromide emulsion containing per kg. 15 g. of DIR compound No. 3; silver application 1.0 g./m.²;
- (8) a silver iodide emulsion, silver application 0.2 g./m.²;
- (9) a silver chloride emulsion containing per kg. 15 g. of the dye-giving compound M and 10 ml. of a 2% sus-

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pension of colloidal silver sulfide; silver application 0.4 g./m.²;

- (10) a green-sensitized silver iodobromide emulsion containing per kg. 12 g. of DIR compound No. 3; silver application 1.2 g./m.²;
- (11) a silver iodide emulsion, silver application 0.2 g./m.²;
- (12) a silver chloride emulsion containing per kg. 20 g. of dye-giving compound F and 10 ml. of a 2% silver sulfide suspension; silver application 1 g./m.²;
- (13) a non-sensitized silver iodide emulsion containing per kg. 10 g. of compound No. 3; silver application 1.2 g./m.².

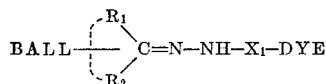
After exposure to an original which is required to be copied, the assembly of the layers is covered with a covering layer which is impermeable to light and which consists of a pigmented cellit support on which a gelatin layer of 6μ has been applied. Before the covering layer and the assembly of photographic layers were pressed together, the covering layer was dipped into the following solution for 3 minutes:

10 g. of N-ethyl-N-β-hydroxyethyl aniline,
0.2 g. of ascorbic acid,
20 g. of potassium carbonate,
0.5 g. of anhydrous sodium sulfite,
0.3 g. of sodium thiosulfate,
water up to 1000 ml.;
pH adjusted to 11.5.

A colored reproduction of the original copy is formed within 3 minutes which can be seen through the transparent support.

What we claim is:

1. In the dye diffusion transfer process for the production of positive color photographic images by imagewise exposing a light-sensitive dye-giving element comprising at least one combination of a first light-sensitive silver halide emulsion layer having associated therewith a non-diffusing DIR compound and a second unexposed developable emulsion layer containing a non-diffusing dye-giving compound, wherein on development a diffusing dye is liberated from the dye-giving compound and transferred to an image-receiving layer at those parts where development of the unexposed developable emulsion has not been inhibited by diffusing development inhibitors split off from the DIR compounds by the action of oxidation products of color developers, the improvement according to which the dye-giving compound is a compound selected from the group consisting of a substituent of the formula of:



wherein

R₁ represents hydrogen, an alkyl group with up to 20 carbon atoms, an aralkyl group, an aryl group or an amino group substituted with alkyl or aryl, in which two alkyl groups attached to the nitrogen may be joined to form a ring;

R₂ represents an alkyl group with up to 20 carbon atoms, an aralkyl group, an aryl group, an acyl group derived from aliphatic carboxylic acids with up to 20 carbon atoms or from aromatic carboxylic acids, or an amino group substituted with alkyl or aryl, in which two alkyl groups attached to the nitrogen may be joined together to form a ring; or

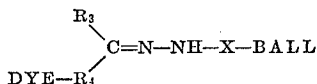
R₁ and R₂ taken together may represent the ring members required to complete an isocyclic or heterocyclic group; at least one of the radicals R₁ and R₂ carries the group BALL;

X₁ represents a sulfonyl group or a carbonyl group;

BALL represents a ballasting photographically inert radical rendering the dye-giving compound resistant to diffusion selected from the group consisting of

straight chain or branched chain aliphatic groups containing from 8 to 20 carbon atoms and said aliphatic group together with isocyclic or heterocyclic groups; said radicals being directly or indirectly connected by one of the following groups: $-\text{CONH}-$, $-\text{SO}_2\text{NH}-$, $-\text{CO}-$, $-\text{SO}_2-$, $-\text{NR}-$ in which R represents a hydrogen atom or an alkyl group, or $-\text{O}-$ or $-\text{S}-$; and

DYE represents a dye radical selected from the group of dyes consisting of azo dyes, anthraquinone dyes, phthalocyanine dyes, indigoid dyes and triphenylmethane dyes; and a substituent of the formula of:



wherein

R_3 represents hydrogen, an alkyl group, an aralkyl group or an aryl group;

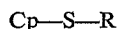
R_4 represents an aryl group, which may be part of the chromophoric system of the dye radical;

X represents a sulfonyl group, a carbonyl group or a single chemical bond;

BALL represents a ballasting photographically inert radical rendering the dye-giving compound resistant to diffusion selected from the group consisting of straight chain or branched chain aliphatic groups containing from 8 to 20 carbon atoms and said aliphatic groups together with isocyclic or heterocyclic groups; said radicals being directly or indirectly connected by one of the following groups: $-\text{CONH}-$, $-\text{SO}_2\text{NH}-$, $-\text{CO}-$, $-\text{SO}_2-$, $-\text{NR}-$ in which R represents a hydrogen atom or an alkyl group, or $-\text{O}-$ or $-\text{S}-$; and

DYE represents a dye radical selected from the group of dyes consisting of azo dyes, anthraquinone dyes, phthalocyanine dyes, indigoid dyes and triphenylmethane dyes.

2. The dye diffusion transfer process according to claim 1 wherein the non-diffusing DIR compound which reacts with oxidation products of the color developer to split off a diffusing development inhibiting substance is a compound of the following formula:

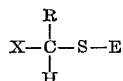


wherein

Cp represents a color coupler radical; and

R represents an organic radical which is split off together with the sulfur atom of the thioether bridge in the reaction with the oxidation products of the color developer forming a diffusing mercapto compound which has a development inhibiting action.

3. The dye diffusion transfer process according to claim 1 wherein the non-diffusing compound which reacts with oxidation products of the color developer to split off a diffusing development inhibiting substance is a compound of the following formula:



wherein

E represents a group which is split off together with the sulfur atom of the thioether bridge in the reaction with oxidation products of the color developer, forming a diffusing mercapto compound which has a development inhibiting action;

R represents

- (1) hydrogen,
- (2) alkyl,
- (3) aralkyl,
- (4) cycloalkyl,
- (5) aryl,

(6) a heterocyclic radical having 5 or 6 ring members, or

(7) the group $-\text{S}-\text{E}$;

X represents one of the following groups which activate the carbon atom to which X, R and $-\text{S}-\text{E}$ are attached:



$-\text{CONH}_2$, $-\text{CONHR}_1$, $-\text{CON}(\text{R}_1)_2$, $-\text{SO}_2\text{R}_1$, $-\text{SO}_3\text{H}$, $-\text{SO}_3\text{OR}_1$, $-\text{SO}_2\text{N}(\text{R}_1)_2$, $-\text{CN}$,

$[-\text{N}(\text{R}_1)_3]^+$

or the group $-\text{S}-\text{E}$;

R_1 represents

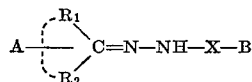
- (1) a saturated or olefinically unsaturated aliphatic radical with up to 18 carbon atoms.
- (2) aryl, or
- (3) a 5-membered or 6-membered heterocyclic radical; two of the substituents R_1 may together represent the ring members required for completing a saturated 5-membered or 6-membered ring which contains nitrogen.

4. The dye diffusion transfer process according to claim 1 wherein the light-sensitive dye-giving element consists of a red-sensitized silver-halide emulsion layer, a green-sensitized silver halide emulsion layer and a blue-sensitive silver halide emulsion layer and, associated with each of these silver halide emulsion layers, a non-diffusing DIR compound which reacts with oxidation products of the color developer to split off a diffusing development inhibiting substance, and an unexposed developable emulsion layer containing a non-diffusing dye-giving compound which reacts with the oxidation products of the developer to split off a diffusing dye, the color of which is complementary to the color of the light to which the associated light-sensitive silver halide emulsion layer is sensitive.

5. The dye diffusion transfer process according to claim 1 wherein after transfer of the dyes, the image-receiving layer is separated from the originally light-sensitive element.

6. The dye diffusion transfer process according to claim 1 wherein the image-receiving layer remains in contact with the original light-sensitive material after the dyes have been transferred.

7. Photographic material for the dye diffusion transfer process, consisting of a dye-giving light-sensitive element arranged on a support, which light-sensitive element consists of at least one combination of a light-sensitive silver halide emulsion layer, and, in combination with this layer, a non-diffusing compound which reacts with oxidation products of the color developer to split off a diffusing development inhibiting substance, and an unexposed developable emulsion layer which contains a non-diffusing dye-giving compound of the following formula:



R_1 represents hydrogen, an alkyl group with up to 20 carbon atoms, an aralkyl group, an aryl group or an amino group substituted with alkyl or aryl, in which two alkyl groups on the nitrogen atom may be joined together to form a ring;

R_2 represents an alkyl group with up to 20 carbon atoms, an aralkyl group, an aryl group, an acyl group derived from an aliphatic carboxylic acid with up to 20 carbon atoms or from an aromatic carboxylic acid, or an amino group substituted with alkyl or aryl, in which two alkyl groups attached to the nitrogen atom may be joined together to form a ring; or

R_1 and R_2 may together represent the ring members required for completing an isocyclic or heterocyclic

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group; at least one of the radicals R_1 and R_2 carries the group A;

X represents a sulfonyl group, a carbonyl group or a single chemical bond;

A represents a photographically inert radical rendering the dye-giving compound resistant to diffusion; and

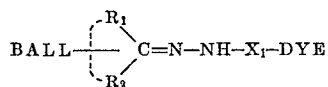
B represents a dye radical; or

A represents a dye radical, either alone or together with R_2 , and

B represents a photographically inert radical rendering the dye-giving compound resistant to diffusion.

8. Photographic material according to claim 7 wherein the unexposed developable emulsion layer contains a compound of the following formula as dye-giving compound:

II



wherein

R_1 represents hydrogen, an alkyl group with up to 20 carbon atoms, an aralkyl group, an aryl group or an amino group substituted with alkyl or aryl, in which two alkyl groups attached to the nitrogen atom may be joined together to form a ring;

R_2 represents an alkyl group with up to 20 carbon atoms, an aralkyl group, an aryl group, an acyl group derived from aliphatic carboxylic acids with up to 20 carbon atoms or from aromatic carboxylic acids, or an amino group substituted with alkyl or aryl, in which two alkyl groups attached to the nitrogen atom may be joined together to form a ring; or

R_1 and R_2 may together represent the ring members required for completing an isocyclic or heterocyclic group; at least one of the radicals R_1 and R_2 carries the group BALL;

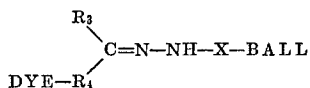
X_1 represents a sulfonyl group or a carbonyl group;

BALL represents a photographically inert radical rendering the dye-giving compound resistant to diffusion; and DYE

DYE represents a dye radical.

9. Photographic material according to claim 7 wherein the unexposed developable emulsion layer contains a compound of the following formula as dye-giving compound:

III



wherein

R_3 represents hydrogen, an alkyl group, an aralkyl group or an aryl group;

R_4 represents an aryl group which may be part of the chromophoric system of the dye radical;

X represents a sulfonyl group, a carbonyl group or a single chemical bond;

BALL represents a photographically inert radical rendering the dye-giving compound resistant to diffusion; and

DYE represents a dye radical, either alone or together with R_4 .

10. Photographic material according to claim 1 which contains, in association with the light-sensitive silver halide emulsion layer, a non-diffusing compound of the following formula which reacts with oxidation products of the color developer to split off a diffusing development inhibiting substance:



wherein

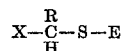
Cp represents a color coupler radical;

R represents an organic radical which is split off together with the sulfur atoms of the thioether bridge

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in the reaction with oxidation products of the color developer, forming a diffusing mercapto compound which has a development inhibiting action.

11. Photographic material according to claim 7 which contains, in association with the light-sensitive silver halide emulsion layer, a non-diffusing compound of the following formula which reacts with oxidation products of the color developer to split off a diffusing substance which inhibits development:



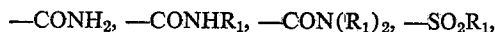
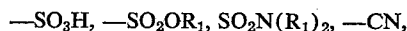
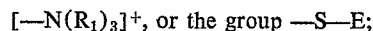
15 wherein

E represents a group which is split off together with the sulfur atom of the thioether bridge in the reaction with oxidation products of the color developer, forming a mercapto compound which has a development inhibiting action;

R represents

- (1) hydrogen,
- (2) alkyl,
- (3) aralkyl,
- (4) cycloalkyl,
- (5) aryl,
- (6) a heterocyclic radical having 5 to 6 ring members, or
- (7) the group $-\text{S}-\text{E}$;

X represents one of the following groups which activate the carbon atom to which X, R and $-\text{S}-\text{E}$ are attached:



R_1 represents

- (1) a saturated or olefinically unsaturated aliphatic radical with up to 18 carbon atoms,
- (2) aryl, or
- (3) a 5-membered or 6-membered heterocyclic radical; two of the substituents R_1 may together represent the ring members required for completing a saturated 5-membered or 6-membered ring which contains nitrogen.

12. Light-sensitive dye-giving element as constituent of a photographic material for the dye diffusion transfer process, which comprises the following layers:

- (1) blue-sensitive silver halide emulsion layer, and, in association with this layer, a non-diffusing DIR compound which splits off a development inhibiting substance in its reaction with oxidation products of color developer;
- (2) unexposed developable emulsion layer containing a non-diffusing dye-giving compound of one of the Formulae I, II and III which splits off a diffusing yellow dye in the reaction with oxidation products of developer;
- (3) green-sensitized silver halide emulsion layer, and, in association with this layer, a non-diffusing DIR compound which splits off a development inhibiting substance in the reaction with oxidation products of color developer;
- (4) unexposed developable emulsion layer containing a non-diffusing dye-giving compound of one of the Formulae I, II and III which splits off a diffusing magenta dye in the reaction with oxidation products of the developer;

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- (5) red-sensitized silver halide emulsion layer, and, in association with this layer, a non-diffusing compound which splits off a diffusing development inhibiting substance on reacting with oxidation products of color developer;
- (6) unexposed developable emulsion layer containing a non-diffusing dye-giving compound of one of the Formulae I, II and III which splits off a cyan dye in the reaction with oxidation products of the developer.

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5 NORMAN G. TORCHIN, Primary Examiner

A. T. SURO PICO, Assistant Examiner

U.S. Cl. X.R.

96—29 D, 77, 95, 109