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Puschel et al.

[11] **3,844,785**
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[54] COLOR PHOTOGRAPHIC DIFFUSION TRANSFER PROCESS AND PHOTOGRAPHIC MATERIAL FOR USE IN THIS PROCESS

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[51] **Int. Cl.**....... **G03c 5/54,** G03c 7/00, G03c 1/40
[58] **Field of Search**........................... 96/3, 29 D, 77

[56] **References Cited**

UNITED STATES PATENTS

3,467,520	9/1969	Puschel et al.	96/53
3,628,952	12/1971	Puschel et al.	96/29 D

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Attorney, Agent, or Firm—Connolly and Hutz

[57] ABSTRACT

For producing color photographic dye diffusion transfer images new dye-giving compounds of formula described hereinafter are used. The compounds are either mobile in alkaline processing solution and are immobilized upon development or the compounds are resistant to diffusion and on development release a mobile dye or dye precursor.

3 Claims, No Drawings

COLOR PHOTOGRAPHIC DIFFUSION TRANSFER PROCESS AND PHOTOGRAPHIC MATERIAL FOR USE IN THIS PROCESS

This invention relates to a color photographic diffusion transfer process in which in order to produce a dye image a light-sensitive material comprising at least one silver halide emulsion layer is imagewise exposed and developed, and a dye which has been rendered diffusible by development is transferred imagewise to an imagereceiving layer, and to a material for carrying out such a process.

In black-and-white photography, it has long been known to produce positive images by developing an imagewise exposed silver halide emulsion layer to form a silver image, the silver halide which has remained undeveloped then being transferred imagewise to an image-receiving layer where it is converted into a positive image, for example by means of a precipitating agent. Attempts have also been made to apply this so-called silver salt diffusion process to color photography but usually only diffusion of silver salts takes place and the dye is generally only produced subsequently by chromogenic development in the receiving layer.

Diffusion processes for the production of color photographic negative or positive images have also become known in which a color-forming coupler, or an already preformed dye diffuses into an image-receiving layer. In one known process, use is made of the fact that the dye produced by chromogenic development is diffusion-fast while the color-forming coupler from which it is formed and which is normally capable of diffusing on account of its comparatively low molecular weight is incorporated in the light-sensitive layer in a diffusion-fast form as so-called "oil-packets," i.e., it is dissolved in droplets of a high boiling, low molecular weight, practically water-insoluble organic solvent. This process has been described, for example, in German Pat. specification Nos. 1,150,278 and 1,272,716. However, due to the nature of the hydrophilic groups required for diffusion and the nature of the developers used, it is necessary to employ very high pH values in this process in order to render the coupler diffusible. This process results in azomethine dyes with all their well-known disadvantages, e.g., their instability and low light-fastness.

Another known process makes use of so-called dye developers, i.e., compounds which contain both a dye group and a group capable of developing silver halide in one and the same molecule. This process has been described, for example, in German Pat. specification No. 1,196,075. However, very complicated materials are required for carrying out this process and again it is necessary to operate at very high pH values on account of the hydrophilic groups which render the substance diffusible, which in this case are generally phenolic hydroxyl groups.

In a third color-photographic diffusion process, which has been described, for example, in German Pat. Specification No. 1,095,115, non-diffusing color-forming couplers are used and a bond which is situated in the coupling position and which by way of an intermediate member links the diffusion-fast coupler group to a diffusible dye or second coupler group or links a ballasting group to a diffusible coupler group is broken in the course of development with color developers. The usual types of couplers commonly used in photography are described there, such as pyrazolinon-(5) derivatives, phenol or α-naphthol derivatives and open chain ketomethylen compounds. By "coupling position" of the coupler molecule is meant, in the case of the pyrazolinone-(5) compounds, the carbon atom in the 4-position, in the case of phenols and α-naphthols also the carbon atom in the 4-position and in the case of open chain ketomethylene couplers, the carbon atom of the methylene group in the grouping CO—CH$_2$—CO.

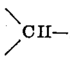
In the process of coupling with oxidized colour developers, the substituent in the coupling position is split off and, depending on the way in which the process is carried out, the resulting product is either a diffusible azomethine dye or, if the coupler part of the molecule is diffusion-fast, a diffusible dye which may also belong to another class of dyes. The diffusible dyes obtained diffuse from the light sensitive layer into an image-receiving layer in close contact with it, where they are fixed by mordanting.

The individual steps of this process have been known for some time, for example the process of imagewise dye transfer is the basis of the technicolor process. In this connection, reference may also be made to the inhibition process of Bela Gaspar. It is also known to apply the principle of (the) splitting off of groups situated in the coupling position of color-forming couplers to the formation of a color image. This has been disclosed, for example in U.S. Pat. No. 2,435,616; 2,453,661 and 2,455,169.

Although the combination of the individual known steps of the process no doubt provides a very interesting and technically progressive combination process for dye diffusion, this process nevertheless has some disadvantages. For example, the diffusing dyes are generally azomethine dyes, to which reference has already been made above, and therefore have only moderate stability and light fastness. Other serious disadvantages also come to light even in cases where the group split off at the coupling position of a diffusion-fast coupler is that of a diffusible dye which belongs to some other class of dyes and may therefore be more light-fast.

The part of the molecule which is split off by oxidative coupling is attached to the "coupling position" by a "connecting group." The following are examples of connecting groups

—Hg—, —O—, —N=N—,



=CH—, —S— or —S—S—

These groups are not found to be all equally advantageous. Some of them, for example the groups —Hg—, —O— and =CH—, are unsuitable in practice because they are split off too slowly. Moreover, in the corresponding patents, e.g., German Pat. No. 1,095,115, the only group which has been specifically mentioned as a breakable bond between the light-fast dye and the diffusion-fast coupler group is the azo bond. However, as is well known, if the azo group is chosen as bridge member then the reaction with oxidized color developer is accompanied by the formation of nitrogen which partly escapes from the layer in the form of microscopic bubbles and interferes with the necessary contact between the layer which produces the dye and the image receiving layer, especially if elevated temperature is employed to accelerate the process.

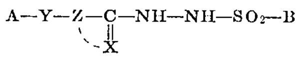
Although the thioether group is known to be split off very readily from the coupling position of couplers in the reaction with oxidized color developers, its use as bridge member between the diffusion-fast coupler and diffusible dye group in this dye diffusion process has certain disadvantages in that mercaptans, which are formed in this reaction, are known to react very readily with silver halide either chemically to form silver mercaptides or physically by adsorption so that they are held by the silver halide. This fact is made use of, for example, when using so-called DIR couplers ("development inhibitor releasing"), but these properties run counter to the requirement for rapid and quantitative diffusion of the liberated dyes. Another dye diffusion material has been described in German OS No. 1,930,215, that makes use of compounds wherein a potentially diffusing dye or a dye precursor group is attached to a ballasting group via a sulfonylamidrazone group. In the process of development, the dye groups are rendered diffusible by reaction with the developer oxidation product and may contribute to the formation of an image in a suitable image-receiving layer.

The sulfonyl amidrazones used as dye-giving compounds in the above mentioned Offenlegungsschrift are, however, generally compounds with a complicated structure and their preparation is often difficult and above all expensive. It is particularly the quaternization of the required N-heterocyclic groups which often gives rise to considerable difficulties if the heterocyclic group at the same time contains a group which confers diffusion fastness.

It is an object of this invention to provide a simple dye diffusion process, combined with a suitable photographic material for carrying it out, which will not have the disadvantages of the processes mentioned above and which is based on readily accessible and inexpensively synthesised compounds.

A color photographic diffusion transfer process has now been found in which the material which contains a dye-giving compound in at least one light-sensitive silver halide emulsion layer or in a hydrophilic colloid layer adjacent thereto is exposed imagewise and developed to produce a colour image, and either the dye-giving compound itself or a diffusible decomposition product obtained from it by development is transferred imagewise as a dye or a dye precursor to an image-receiving layer.

The process is characterized by using a dye-giving compound of the following general formula



$$A-Y-Z-\underset{\substack{\| \\ X}}{C}-NH-NH-SO_2-B$$

in which

A denotes the group of a dye or dye precursor or:

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

B denotes an aliphatic or aromatic group, preferably an alkyl group containing 1 to 4 carbon atoms or phenyl in cases where A denotes the group of a dye or dye precursor or:

the group of a dye or dye precursor in cases where A is a photographically inert radical rendering the dye-giving compound resistant to diffusion

X denotes oxygen, sulfur or an imino group (—NR, wherein R denotes hydrogen or an alkyl group);

Y denotes a chemical bond or a linking group such as oxygen, sulfur or an imino (—NR—), carbonyl (—CO—), sulfonyl (—SO_2—), sulfonamide (—SO_2—NR—) or carbonamide (—CO—NR—) group in which group R denotes hydrogen or alkyl;

Z denotes a chemical bond between Y and C or taken together with C and X it denotes a heterocyclic group comprising a 5-membered or 6-membered heterocyclic ring in which X denotes nitrogen.

Suitable heterocyclic groups which are formed by Z, C and X are: Nitrogen-containing heterocyclic rings to which benzene rings may be attached by condensation, for example the oxazole, thiazole, imidazole, pyrrole, oxadiazole, thiadiazole, triazole, pyrazole, pyridine, pyrimidine, pyrazine and triazine ring. In addition to the substituent A which may, of course, also contain water-solubilizing groups, other water-solubilizing groups such as sulfo or carboxyl groups may also be attached to the heterocyclic group either directly or, for example, by way of a short chain alkyl group.

The dye groups may in principle be groups from any classes of dyes, provided they are sufficiently diffusible to be able to diffuse through the layers of the light-sensitive material into the image-receiving layer. On account of this requirement, the dye groups preferably contain one or more water-solubilizing groups. The water-solubilizing groups may be, for example, carboxyl groups, sulfo groups, and aliphatic or phenolic hydroxyl groups. The following are examples of dyes which are particularly suitable for the process according to the invention: Azo dyes, anthraquinone dyes, phthalocyanine dyes, indigoid dyes and triphenylmethane dyes.

By groups of dye precursors are meant groups which in the course of photographic processing, either in one of the usual steps of the process or in additional steps, are converted into dye groups be it by oxidation by coupling or by any other reaction wherein, for example, a potentially preformed but temporarily blocked auxochromic group in a chromophoric system is liberated e.g., by saponification. Dye precursors in this sense may be leuco dyes in the course of processing. In cases where it is not important to distinguish between dye groups and groups of dye precursors, the term "dye group" will be used to cover both. Similarly, the term "dye" will hereinafter be used to mean both dyes and dye precursors.

By groups rendering the dye-giving compound resistant to diffusion are meant groups which enable the compounds according to the invention to be incorporated in a diffusion-fast form in the hydrophilic colloids normally used in photographic materials. Groups which are particularly suitable for this purpose are organic groups which may generally contain linear or branched aliphatic groups and optionally also isocyclic or heterocyclic aromatic groups. The aliphatic part of these groups generally contains 8 to 20 carbon atoms. These groups are attached to the remaining part of the molecule either directly or indirectly, e.g., through one of the following groups: —CONH—, —SO_2NH—, —CO—, —SO_2—, —NR— (R denotes hydrogen or alkyl), —O— or —S—. The group rendering the dye-giving compound resistant to diffusion may in addition contain water-solubilizing groups such as sulfo groups or carboxyl groups and these may also be in the anionic form. Since the diffusion properties depend on the molecular size of the whole compound, it is sufficient in certain cases, e.g. if the whole molecule used is large enough, to use only short chain groups as such groups which render resistant to diffusion.

The dye diffusion transfer process may principally be carried out in two different, equally advantageous forms with the compounds according to the invention, depending on whether the dye group is represented by A or B in the given compound.

If B denotes a dye group then A represents a group rendering the dye-giving compound resistant to diffusion. In this preferred embodiment of the invention, the dye-giving compounds which are originally firmly fixed in the layer are split by the reaction with developer oxidation products so that the dyes or dye precursors are released. Since the dyes generally contain one or even more solubilizing groups, they are capable of diffusing into the image-receiving layer where they can be fixed by means of a dye mordant. The group rendering resistant to diffusion remains behind in the emulsion layer. Since in this embodiment of the process the diffusible dyes are liberated only in the exposed areas, a negative of the original is obtained in the image-receiving layer if usual negative silver halige emulsions are employed. In this case, the dye-giving compounds should be fixed with as high diffusion fastness as possible in the layers. Since the resistance to diffusion decreases with increasing number of solubilizing groups, the dye-giving compounds should contain as few such solubilizing groups as possible. On the other hand, production and processing of the photographic materials is facilitated if the dye-giving compounds are sufficiently soluble in aqueous-alkaline media. Moreover, the dyes which have been split off should diffuse rapidly and quantitatively, which again requires a sufficiently large number of solubilizing groups. A suitable balance should therefore be struck between the size of the groups rendering resistant to diffusion and the number of solubilizing groups in order that on the one hand the dye-giving compounds will be sufficiently diffusion-fast and on the other hand the dyes split off will diffuse sufficiently rapidly.

It is therefore particularly advantageous in this embodiment of the process that the process may also be carried out with dye-giving compounds in which the dye groups contain no solubilizing groups or a smaller number of such groups than is necessary for diffusion because a solubilizing group is latently present in the molecule, this group being a sulphinic acid group formed from the sulfonyl group when the dye is split off by reaction with the developer oxidation products, and remaining in the dye portion (B) of the molecule. In this way, rapid diffusion of the dye which is split off is achieved together with extreme insolubility and hence resistance to diffusion of the dye-giving compounds incorporated in the layer.

In a second particular embodiment of the process, dye-giving compounds in which A denotes a dye group and B preferably a phenyl or short chain alkyl group are used. These compounds do not contain a group which renders resistant to diffusion and are therefore diffusible in photographic layers in alkaline media without first having to undergo a reaction. When these layers are developed in the presence of a diffusion fast developer, the dye-giving compounds which in this case may be identical with the image dyes react with the developer oxidation product only in the exposed areas of the layer and are thereby fixed imagewise. In the unexposed and therefore undevelopable parts of the layer, the dye-giving compounds remain diffusible and can be transferred to an image-receiving layer where, if a normal, negative silver halide emulsion is used, they give rise to a positive color image of the original without requiring a photographic reversal process.

The following are examples of dye-giving compounds which are suitable for this invention:

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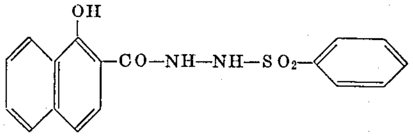

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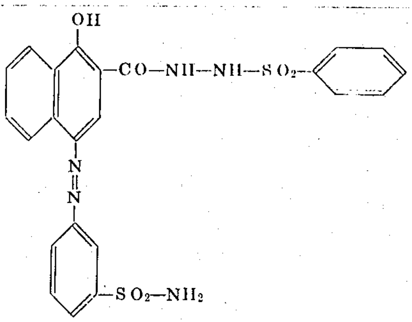

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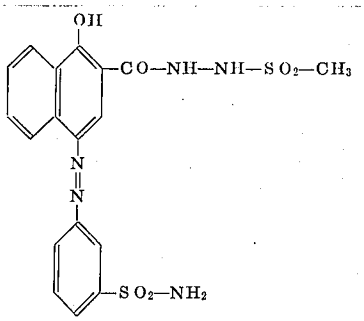

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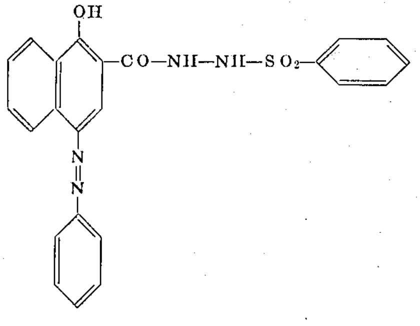

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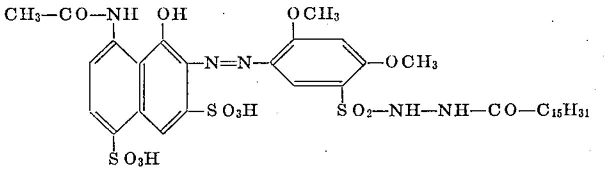

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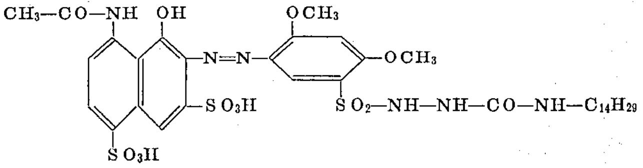

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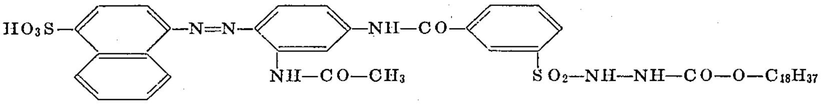

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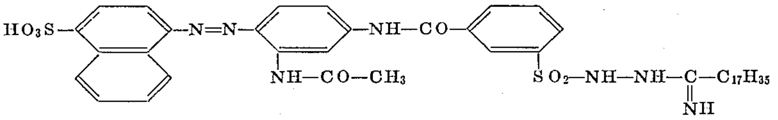

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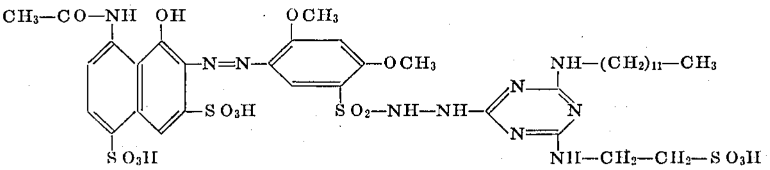

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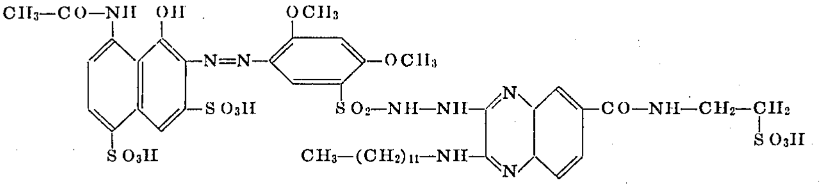

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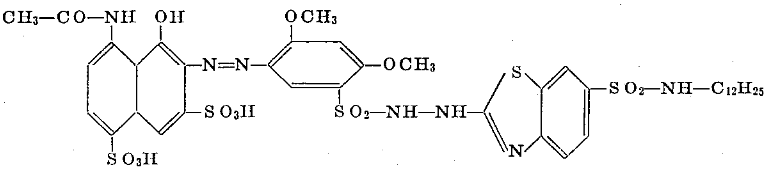
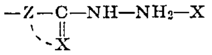


Synthesis of the dye-giving compounds according to the invention may be carried out by conventional methods. The starting compounds used are preferably compounds which already contain the group



$$-Z-\underset{\underset{X}{\|}}{C}-NH-NH_2-X$$

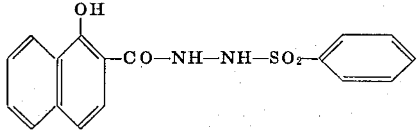
and Z having the meaning given above, e.g., carboxylic acid hydrazides or heterocyclic hydrazine compounds. They are reacted with a suitable sulfonyl halide, preferably in the presence of basic condensing agents such as pyridine, one of the two reactants containing a dye group or a dye precursor group. If it contains a dye precursor group, the product obtained from the reaction may either itself be used as a dye-giving compound according to the invention, in which case the color producing reaction takes place in the course of the photographic process of the color photographic material, either during or after diffusion, or if such a colorless dye-giving compound contains a molecular group which is capable of coupling or any other color-producing reaction, it may first be converted into a colored dye-giving compound, e.g., by coupling with a diazonium salt. The synthesis will be explained with the aid of examples given below.

DYE-GIVING COMPOUND 1

a. 1-Hydroxy-2-naphthoic acid hydrazide

52 g of phenyl 1-hydroxy-2-naphthoate are suspended in 300 ml of ethanol and added to a refluxing solution of 20 ml of hydrazine hydrate in 100 ml ethanol. After heating for 30 minutes, the reaction mixture is left to stand overnight. The precipitate is suction filtered, washed with ethanol and dried on a steam bath. Yield: 33 g m.p.: 210°–213°C (decomposition)

b. DYE-GIVING COMPOUND 1



20 g of the compound obtained under a) are suspended in 150 ml of dry pyridine. 17.6 g of benzene sulfonyl chloride are added dropwise at room temperature and the suspension is stirred for 3 hours and then left to stand overnight. The slight precipitate which forms is removed by suction filtration. About 500 ml of water are added to the mother liquor and the supernatant liquid is then decanted from the oil which precipitates. The oil is again triturated with water. The crystalline precipitate is suction filtered and dried. Yield: 34.7 g M.p.: 230°C (decomposition).

DYE-GIVING COMPOUND 2

8.5 g of 3-aminobenzene sulfonamide are suspended in 15 ml of concentrated hydrochloric acid to which 30 ml of water are then added. The reactant dissolves at 70°C. The solution is cooled to 0°C and diazotized with a solution of 3.8 g of $NaNO_2$ in 10 ml of water. After stirring for one hour, the excess nitrite is destroyed with amidosulfonic acid. The resulting solution is added dropwise at room temperature to a solution of 17.0 g of dye-giving compound No. 1 in 100 ml of pyridine with stirring and the pH is kept at 8 to 9 with concentrated sodium hydroxide solution. After stirring for 30 minutes, the solution is poured on to a mixture of 100 g of ice and 130 ml of concentrated hydrochloric acid. The precipitate is suction filtered, washed with water and dried. Yield: 26.0 g M.p. 185°C (decomposition).

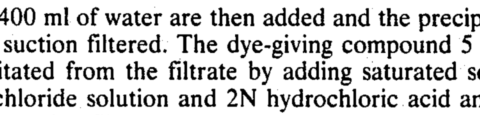
DYE-GIVING COMPOUND 5

a. $C_{15}H_{31} - CO\,NH - NH_2$

130 g of hydrazine hydrate are introduced into 370 ml of water. 54.9 g of palmitic acid chloride are added dropwise at room temperature. After stirring for 30 minutes. the precipitate is suction filtered, washed with water, dried and recrystallized from ethanol. The bisacyl hydrazine which forms at the same time is filtered from the boiling ethanolic solution. Yield: 25 g M.p.: 105°–108°C.

b. DYE-GIVING COMPOUND 5

6.35 g of a dye sulfobromide of the following formula I



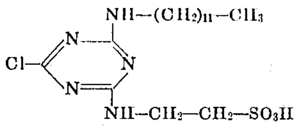
I.

are added to a solution of a 2.48 g of palmitic acid hydrazide in 100 ml of pyridine. The mixture is heated to 60°–70°C and the same quantity of dye sulfobromide I is added again after one hour and the mixture again heated for 30 minutes. The mixture is left to stand overnight, 400 ml of water are then added and the precipitate is suction filtered. The dye-giving compound 5 is precipitated from the filtrate by adding saturated sodium chloride solution and 2N hydrochloric acid and is then suction filtered.

The sulfobromide of the formula I has been prepared starting with 2,4-dimethoxy-5-aminobenzene sulfinic acid by diazotization and coupling with 8-acetamino-1-hydroxy-3,5-disulfonaphthalene according the usual methods of the azo chemistry and subsequent reaction of the sulfinic acid obtained with bromine in aqueous solution. Reference is being made to Houben-Weyl, "Methoden der Organischen Chemie," Vol IX (1955) p. 586 and to German Offenlegungsschrift 2 105 063. Yield: 2.8 g M.p. above 300°C.

DYE-GIVING COMPOUND 9

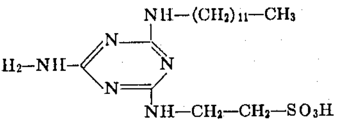
a) II



18.5 g of cyanuric acid chloride are dissolved in 100 ml of acetone and then poured on to a mixture of 200 ml of water and 200 g of ice with stirring. 70 g of a neutral solution of 12.5 g of aminoethane sulfonic acid in water are added dropwise to the suspension at 0° to 5°C in the course of one hour and at the same time the suspension is kept at pH 6 by the addition of 10 percent sodium carbonate solution. It is then stirred for one hour at pH 6.5 and clarified by removing the slight residue formed. 18 g of dodecylamine in 50 ml of acetone are added to the solution and the solution is adjusted to pH 8 with 5 N HCl, heated to 40°C and kept at pH 7 for one hour with 5N sodium hydroxide solution. The mixture is adjusted to pH 1 and the precipitate is suction filtered and washed with water. The residue is stirred up in acetone, suction filtered, washed with acetone and dried.
Yield: 23 g.

b)

III



10.5 g of 2-chloro-4-dodecylamino-6-β-sulfoethylamino-1,3,5-triazine (Compound II) in 90 ml of water and 10 ml of ethanol are boiled under reflux together with 10 g of hydrazine hydrate for 2 hours. After cooling, the reaction product is precipitated with 10 g of NaCl and suction filtered. The precipitate is dissolved in 50 ml of warm water at pH 10 and then precipitated by adjusting to pH 2–3 with 5N HCl, suction filtered and washed with water. It is then stirred up with methanol, again suction filtered and dried.
Yield: 3.7 g.

c. Dye-giving compound 9

4.5 g of the dye sulphobromide I used for the synthesis of dye-giving compound 5 are gradually sprinkled into a solution of 2.7 g of the above compound III in 160 ml of water and 8 ml of pyridine with stirring. After 30 minutes' stirring, 80 ml of methanol and 4 g of NaCl are added to the reaction solution and the solution is heated until the precipitate dissolves and is then left to cool with stirring. The precipitate is suction filtered and washed with a mixture of 2 parts of 2.5 percent NaCl solution and 1 part of methanol. The residue is stirred up in acetone, suction filtered, washed with acetone and dried. 6 g of the resulting dye were stirred up in 30 ml of dimethylformamide and suction filtered to remove undissolved constituents. The dye was then precipitated from the solution with 60 ml of acetone. It is suction filtered, washed with acetone and dried.
Yield: 5.5 g.

The materials required for carrying out the process according to the invention basically consist of two elements: A light-sensitive material which contains at least one silver halide emulsion layer and at least one of the dye-giving compounds according to the invention, and a light insensitive image receiving material which may contain a dye mordant and which serves to take up the diffusing dye.

The usual silver halide emulsions are suitable for this invention. The silver halides used may be 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 photographic layers is preferably gelatin but this may be partly or completely replaced by other natural or synthetic binders. Suitable natural binders are e.g. alginic acid or its derivatives such as salts, esters or amides, cellulose derivatives such as carboxymethylcellulose, alkylcelluloses such as hydroxyethyl cellulose, starch or derivatives of starch such as the ethers or esters or carrageenates. Polyvinyl alcohol, partly saponified polyvinyl acetate, polyvinyl pyrrolidone and the like are suitable synthetic binders.

The emulsions may also be chemically sensitized, e.g. by the addition of sulfur compounds at the chemical ripening stage, for example allyl isothiocyanate, allylthiourea, sodium thiosulfate and the like. Reducing agents may also be used as chemical sensitizers, e.g., the tin compounds described in Belgian Pat. specification Nos. 493,464 and 568,687, polyamines such as diethylene triamine or amino methane sulphinic acid derivatives, e.g., as described in Belgian Pat. specification No. 547,323.

Noble metals such as gold, platinum, palladium, iridium, ruthenium or rhodium and compounds of these metals are also suitable chemical sensitizers. This method of chemical sensitization has been described in the article by R. Koslowsky, Z. Wiss. Phot. 46, 65–72 (1951).

The emulsions may also be sensitized with polyalkylene oxide derivatives, e.g. with a polyethylene oxide which has a molecular weight of between 1,000 and 20,000 or with condensation products of alkylene oxides and aliphatic alcohols, glycols, cyclic dehydration products of hexitols, alkyl substituted phenols, aliphatic carboxylic acids, aliphatic diamines and amides. The condensation products should have a molecular weight of at least 700 and preferably more than 1000. The sensitizers may, of course, be combined for the purpose of achieving special effects, as described in Belgian Pat. specification No. 537,278 and in British Pat. specification No. 727,982.

The emulsions may also be spectrally sensitized, e.g., with the usual monomethine or polymethine dyes such as acid or basic cyanines, hemicyanines, streptocyanines, merocyanines, oxonoles, hemioxonoles, styryl dyes and others as well as with trinuclear or higher nuclear methine dyes, for example rhodacyanines or neocyanines. Sensitizers of this kind have been described, for example, in the work by F. M. Hamer "The Cyanine Dyes and Related Compounds" (1964), Interscience Publishers, John Wiley and Sons.

The emulsions may contain the usual stabilizers, e.g. homopolar or salt type compounds of mercury which contain aromatic or heterocyclic rings, such as mercaptotriazoles, simple mercury salts, sulphonium mercury double salts and other mercury compounds. Azaindenes are also suitable stabilizers, particularly tetra- or penta-azaindenes and especially those which are substituted with hydroxyl or amino groups. Compounds of this kind have been described in the article by Birr, Z. Wiss. Phot. 47, 2 – 58 (1952). The various other suitable stabilizers include heterocyclic mercapto compounds, e.g., phenylmercaptotetrazole, quaternary benzothiazole derivatives, benzotriazole and the like.

The emulsions may be hardened in the usual manner, for example with formaldehyde or halogenated aldehydes which contain a carboxyl group, such as mucobromic acid, diketones, methane-sulphonic acid esters, dialdehydes and the like.

The emulsions used may be conventional negative emulsions or direct positive emulsions, e.g., those which have a high sensitivity in the interior of the silver halide grains or those which operate by the solarisation principle. The choice of emulsions depends on the purpose for which they are intended. If, for example, a positive image is to be produced from a color negative then negative emulsions are used. If, on the other hand, a positive image is to be produced from a positive original, e.g., from a color diapositive, then direct positive emulsions may be used. On the other hand, positive copies can also be obtained from positive originals by means of a conventional negative silver halide emulsion if, as has already been mentioned above, the dye-giving compounds used are of the kind which do not become diffusion fast until they have reacted with developer oxidation products, in which case the transfer of dye takes place only in the non light struck image areas.

A positive image may, of course, also be obtained by reversal development of a negative emulsion. Color images may be obtained from a material in which the light-sensitive element contains only one light-sensitive layer and, for example, only one dye-giving compound according to the invention.

In general, however, the materials used for producing multicolored images are multilayered light-sensitive photographic materials which contain at least three separate silver halide emulsion layers, for example one which is sensitive to red light, one which is sensitive to green light and one which is sensitive to blue light. Each of the said light-sensitive layers are in close contact with one of the dye-giving substances according to the invention.

The close contact between dye-giving compound and silver halide required for achieving the desired effect can be obtained by introducing the dye-giving compound into the silver halide emulsion layers from aqueous alkaline solutions, if desired making use of any water-solubilizing groups present. Alternatively, the dye-giving compounds may be introduced into the layers by one of the known emulsification processes. Such processes have been described, for example, in British Pat. specification Nos. 791,219 and 1,099,414 to 1,099,417. In another embodiment of the process it may be desired, for example, to incorporate the dye-giving compounds together with silver halide and optionally also developing agents in the layer in the form of so-called microcapsules, in which case two or more differently sensitized light sensitive silver halide emulsions and the corresponding dye-giving compounds may be combined in a single layer in the form of so-called mixed grain emulsions as described, for example, in U.S. Pat. No. 2,698,794. The dye-giving compounds may be incorporated in a light-sensitive layer or in a hydrophilic colloid layer adjacent thereto, for example the red sensitive layer is associated with a dye-giving compound which gives rise to a cyan dye, the green sensitive layer is associated with a dye-giving compound which gives rise to a magenta dye and the blue sensitive layer with a dye-giving compound which gives rise to a yellow dye. The multi-layered material may also contain interlayers in which other substances may be accommodated, e.g. filter dyes, white couplers or antioxidants, these interlayers serving to restrict the activity of the developer oxidation products to their corresponding light-sensitive layer. The layers of the light sensitive material may also, as already indicated, contain developing agents such as conventional color developers of the p-phenylenediamine series but also other developers, for example hydroquinone, N-methylaminophenol, pyrocatechol or phenidone. The developers may be incorporated in the layer either as free molecules or in the form of their salts. Since the developing agents should not become active before the development process proper begins, they should as far as possible be incorporated in a diffusion-fast form, for example they may be accommodated in the layer in the form of the packets already mentioned above. Another possibility lies in the use of so-called "masked developers," i.e., developer derivatives which are not themselves developers but liberate the developers by a decomposition reaction which may be initiated e.g. by heat or by alkalies. Such masked developers and their use in photographic layers have been described, for example, in German Pat. specification No. 1,246,406, German Auslegeschrift No. 1,019,560, British Pat. specification Nos. 632,836; 691,815; 783,887; 2,069,061 and 1,114,277 and in U.S. Pat. Nos. 3,243,294 and 2,342,599.

Developing agents which are not only incorporated in a diffusion-fast form in the emulsion layers but also remain diffusion-fast during photographic processing, i.e., in aqueous alkaline media, are preferred for that embodiment of the process in which the dye-giving compounds are diffusible and are transferred to the image receiving layer in the unexposed areas to form a positive image while they are fixed in the exposed parts of the layer by reaction with developer oxidation products, Such developers are known. Developers which contain groups rendering resistant to diffusion have been described, for example, in German Offenlegungsschrift No. 1,931,057.

The light-insensitive material generally consists of any layer support, e.g. a transparent film or suitable paper, for example a paper backed with a layer of synthetic resin, and a layer of binder which constitues the image receiving layer and which may contain a dye mordant to fix the diffusing dyes.

The mordants used for acid dyes are preferably long chain quaternary ammonium or phosphonium compounds or ternary sulphonium compounds, e.g., those described in U.S. Pat. specification Nos. 3,271,147 and 3,271,148. Certain metal salts and their hydroxides which form sparingly soluble compounds with acid dyes may also be used.

The dye mordants are dispersed in one of the usual hydrophilic binders in the receiving layer, e.g., in gelatin, polyvinyl pyrrolidone, completely or partly hydrolysed cellulose esters and the like. Some binders, of course, are capable of functioning as mordants, especially those which consist of polymers of nitrogen-containing quaternary bases, e.g., polymers of N-methyl-2-vinylpyridine as described, for example, in U.S. Pat. No. 2,484,430, or polymers of aminoguanidine derivatives of alkylvinylketones as described e.g. in U.S. Pat. No. 2,882,156 but in general, other binders, e.g. gelatine would be added to the last mentioned mordanting binders.

The image receiving layer may in addition contain other additives, especially in cases where the groups A and B of the dye-giving compound according to the invention are not dye groups but groups of dye precursors because in that case the dye precursors transferred to the image receiving layer must be converted into the ultimate image dye by a reaction which takes place either in the image receiving layer or during the transfer of the product into this layer. These additives may be, for example, oxidizing agents to oxidize leuco dyes or to bring about oxidative coupling of color-forming couplers with color developing agents. The latter may also be present in the image receiving layer or they may be available in the processing substance.

To obtain multicolored images by the process according to the invention, the light sensitive material which has been exposed behind a colored original may first briefly be dipped into a developer solution and then brought into effective contact with the light insensitive receiving material which has also previously been dipped into a developer solution. Silver halide is reduced in the exposed areas. The developer oxidation product which is formed in the image areas reacts with the dye-giving compounds according to the invention which are then either split to liberate diffusible dyes or fixed in the image areas of the emulsion layer. In the former case, the dyes diffuse from the exposed areas and form a negative image in the image receiving layer. In the case where the dye-giving compounds are themselves diffusible, they are only transferred to the image receiving layer in the unexposed areas thus forming a positive image.

By effective contact is meant that the contact enables diffusion of the dye which has been split off to take place between the light sensitive material and the image receiving layer. This does not exclude the possibility that the layers of light sensitive material containing the dye-giving substances according to the invention and the image receiving layer may be separated from each other by colloid layers, provided diffusion of the dyes or dye precursors which have been split off is still ensured.

According to another embodiment of the process, the two elements may be arranged above one another on the same layer support. In that case, the layer support carries first the image receiving layer, which may contain a dye mordant in a binder, and then above this the various layers of the light sensitive material. After exposure and development and when the dyes which have been rendered soluble by development in the image areas have diffused into the underlying image receiving layer, the light sensitive layers may be washed off. Readily soluble emulsions are generally used in this case, for example emulsions based on polyvinyl alcohol or alkali soluble cellulose ether phthalate. The liquid or pasty mixtures required for initiating the process of development may, of course, be accommodated in breakable containers or containers which are easily torn open and which may be arranged, for example, between the light sensitive material and the light insensitive image receiving layer as described, for example, in U.S. Pat. Nos. 2,968,244; 2,559,643; 2,647,049; 2,661,293; 2,698,798 and 2,774,668. Such a combined material is more particularly suitable for self-processing cameras. In that case, the containers for the developer and activator solutions are so arranged and designed that the contents will be released in a suitable quantity for development and formation of diffusing dyes as described after exposure.

The light-sensitive element and image receiving material may also be combined to form an integral film unit as described, for example, in U.S. Pat. Nos. 3,415,644; 3,415,645 and 3,415,646 or in German OS No. 2,052,145. In that case, the light-sensitive element and the image receiving material are arranged between two transparent supports which are firmly connected together or between a transparent support and an opaque support and remain firmly united even after development. If desired, a light-impermeable, reflecting layer which is permeable to alkaline liquids and diffusing dyes may be arranged between the light-sensitive element and the image receiving material or a liquid which contains a clouding agent may be pressed in between these layers to form such a light-reflecting layer after exposure.

The developers may be the conventional color developers used in color photography, e.g., derivatives of p-phenylenediamine having at least one primary amino group. It is, however, a particular advantage of the process acccording to the invention that the choice of developing agents is not restricted to the usual color developers but black-and-white developers may also be used, e.g. 4-aminophenol, 4-methylaminophenol, 3-methyl-4-aminophenol or pyrocatechol and its derivatives.

The developer baths used for the process according to the invention may be, for example, the usual baths used in conventional development processes, e.g., in color photography but it is possible to provide the conditions for optimum diffusion by suitable variation of the mineral salt content of the baths, the pH, the viscosity and the addition of organic solvents. This generally only requires a few routine preliminary tests.

EXAMPLE 1

A color photographic material is prepared by applying the following layers successively to a layer support of cellulose triacetate:

1. a 2 percent aqueous gelatine solution containing per kg 10 g of compound No. 4, 1 g of saponin and 0.1 g of 1,3,5-tris-acryloylhexahydro-1,3,5-triazine; layer thickness 2μ
2. a silver chlorobromide emulsion containing per kg 55 g of silver (6 mols percent of this in the form of silver chloride), 25 mg of a green sensitizer (Dye 13 of German PS No. 1,177,481), 1.5 g of saponin, 0.5 g of 1,3,5-tris-acryloylhexahydro-1,3,5-triazine and 25 g of N-n-octadecyl-N-β-sulfoethyl-p-phenylenediamine per kg; silver application 0.7 g/m^2.

The film is exposed behind a step wedge and then developed by dipping it for 30 seconds into an aqueous activator solution containing 30 g of potassium carbonate and 0.1 g phenidone per litre at 24°C and it is then brought into contact for 3 minutes with an image-receiving material which contains a dye mordant. The image-receiving material consists of a white pigmented cellulose triacetate support coated with a 10μ thick coating of a solution of 20 g of cetyl trimethylammonium bromide in 1 litre of 5 percent aqueous gelatine solution. After removal of the light-sensitive material, a positive, magenta reproduction of the original is found in the image-receiving material.

EXAMPLE 2

A green sensitive iodide-containing silver bromide emulsion containing per kg 50 g of silver (of which 3 mols percent are in the form of silver iodide), 30 mg of dye No. 13 from German PS No. 1,177,481, 0.53 g of saponin, 0.25 g of 1,3,5-tris-acryloyl-hexahydro-1,3,5-triazine and 25 g of compound No. 5 are applied to a layer support of cellulose triacetate; silver application 0.9 g/m^2. The material is exposed and developed as in Example 1, using the following developer solution:

1 g of sodium sulphite,
10 g of N-ethyl-N-β-hydroxyethyl-p-phenylenediamine,
20 g of potassium carbonate
2 g of sodium hydroxide
made up to 1000 ml with water.

A negative magenta copy of the original is obtained.

EXAMPLE 3

A result similar to that in Example 2 is obtained (negative magenta image) when compound No. 5 is replaced by an equal quantity of compound No. 6.

EXAMPLE 4

The following layers are applied successively to a layer support of cellulose triacetate:

1. A green sensitive iodide-containing silver bromide emulsion as in Example 2 but using 25 g of compound No. 9 instead of compound No. 5
2. a 5 percent aqueous gelatin solution containing per kg 5g of pyrocatechol, 0.5 g of phenidone and 0.3 g of saponin per kg; layer thickness 1.5μ.

The film is exposed through a step wedge and then developed for 2 minutes by distributing an activator paste of the following composition between the film and the image receiving material (as in Example 1):

20 g of hydroxyethylcellulose
10 g of sodium carbonate
10 g of sodium hydroxide
made up to 1000 ml with water.

A negative copy of the original is obtained.

We claim:

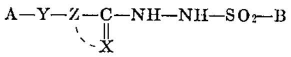
1. The photographic dye diffusion transfer process comprising the steps of

a. imagewise exposing a photographic material having at least one silver halide emulsion layer and uniformly distributed therein or in an hydrophilic colloid layer adjacent thereto a dye-giving compound

b. developing the material to produce therein an imagewise distribution of developer oxidation products

c. reacting said imagewise distribution of developer oxidation products with said dye-giving compound to produce an imagewise distribution of diffusible dye or dye precursor by
either immobilizing the dye-giving compound where said dye-giving compound is diffusible prior to development or splitting the dye-giving compound to liberate a diffusible dye or dye precursor where said dye-giving compound is resistant to diffusion prior to development and

d. transferring the imagewise distribution of diffusible dye or dye precursor to an image-receiving layer, wherein the dye-giving compound is of the following formula:



$$A-Y-Z-\underset{\substack{\| \\ X}}{C}-NH-NH-SO_2-B$$

in which

A represents the group D or E as defined hereinafter;

B represents either an aliphatic or aromatic group when A is the group D or the group D when A is the group E;

D represents a group of a dye or dye precursor;

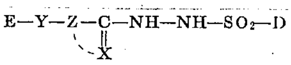
E represents a photographically inert radical rendering the dye-giving compound resistant to diffusion;

X represents oxygen, sulfur, or an imino group

Y represents a connecting member selected from the group consisting of a chemical bond, —O—, —S—, —NR—, —CO—, —SO_2—, —SO_2NR— and —CONR— wherein R denotes hydrogen or alkyl;

Z represents a chemical bond between Y and the carbon atom to which X is attached, or together with said carbon atom and X a heterocyclic group comprising a 5- or 6-membered heterocyclic ring in which X denotes nitrogen.

2. The process of claim 1, wherein the dye-giving compound which is resistant to diffusion prior to development and capable of liberating on development a diffusible dye or dye precursor corresponds to the following formula



$$E-Y-Z-\underset{\substack{\| \\ X}}{C}-NH-NH-SO_2-D$$

in which

D represents a group of a dye or dye precursor;

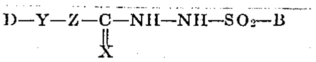
E represents a photographically inert radical rendering the dye-giving compound resistant to diffusion;

X represents oxygen, sulfur, or an imino group

Y represents a connecting member selected from the group consisting of a chemical bond, —O—, —S— —NR—, —CO—, —SO_2—, —SO_2NR— and —CONR— wherein R denotes hydrogen or alkyl;

Z represents a chemical bond between Y and the carbon atom to which X is attached, or together with said carbon atom and X a heterocyclic group comprising a 5- or 6-membered heterocyclic ring in which X denotes nitrogen.

3. The process of claim 1 wherein the dye-giving compound which is diffusible prior to development and capable of being immobilized on development corresponds to the following formula:



$$D-Y-Z-\underset{\substack{\| \\ X}}{C}-NH-NH-SO_2-B$$

in which

B represents either an aliphatic or aromatic group when A is the group D or the group D when A is the group E;

D represents a group of a dye or dye precursor;

X represents oxygen, sulfur, or an imino group

Y represents a connecting member selected from the group consisting of a chemical bond, —O—, —S—, —NR—, —CO—, —SO_2—, —SO_2NR— and —CONR— wherein R denotes hydrogen or alkyl;

Z represents a chemical bond between Y and the carbon atom to which X is attached, or together with said carbon atom and X a heterocyclic group comprising a 5- or 6-membered heterocyclic ring in which X denotes nitrogen.

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