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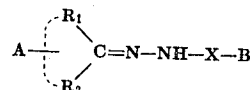
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[33] **Germany**
[31] **P 19 30 215.9**

[54] **PHOTOGRAPHIC DIFFUSION TRANSFER**
MATERIALS AND PROCESSES UTILIZING
BALASTED HYDRAZONE COMPOUNDS TO
RELEASE MOBILE ACID DYES FOR TRANSFER
11 Claims, No Drawings

[52] U.S. Cl. **96/3,**
96/29, 96/76 C, 96/99, 260/240
[51] Int. Cl. **G03c 7/00**
[50] Field of Search **96/3, 100,**
29 D, 9, 99

[56] **References Cited**
UNITED STATES PATENTS
3,443,940 5/1969 Bloom et al. 96/3
Primary Examiner—Norman G. Torchin
Assistant Examiner—Alfonso Suro Pico
Attorney—Connolly and Hutz

ABSTRACT: In a color photographic diffusion transfer process are used diffusion-resistant dye-giving compounds, capable of forming diffusible acid dyes on reaction with oxidation products of black-and-white and color-forming developers and having the formula:



wherein
R₁ represents hydrogen, alkyl, aralkyl or amino;
R₂ represents alkyl, aralkyl, aryl, acyl or amino, or
R₁ and R₂ together represent the ring members required to complete an isocyclic or heterocyclic ring;
X represents sulfonyl, carbonyl or a single chemical bond;
A represents a radical rendering resistant to diffusion, and
B represents a dye radical; or
A represents a dye radical and
B represents a radical rendering resistant to diffusion.

PHOTOGRAPHIC DIFFUSION TRANSFER MATERIALS AND PROCESSES UTILIZING BALASTED HYDRAZONE COMPOUNDS TO RELEASE MOBILE ACID DYES FOR TRANSFER

A PHOTOGRAPHIC DYE DIFFUSION TRANSFER PROCESS AND A CORRESPONDING PHOTOGRAPHIC MATERIAL

This invention relates to a photographic dye diffusion transfer process in which at least one silver halide emulsion layer of a photosensitive material is exposed and developed to produce a color image in which process a dye rendered diffusible through development is transferred at least in part to form an image on a receiving layer. The invention also relates to a photosensitive material for carrying out this process.

It has long been known in black-and-white photography that to produce direct positive pictures and exposed silver halide emulsion layer can be developed to form a negative silver image and that portion of the silver halide which remains undeveloped can be transferred imagewise to a receiving layer where it is converted into a positive silver image, for example by a precipitant. Efforts have been made to use these so-called silver salt diffusion processes in color photography. Usually, it is only a diffusion of silver salts which occurs in this case, whereas the dye is formed in the receiving layer through chromogenic development.

Furthermore, diffusion processes for producing color photographic negative or positive images are already known in which a color-forming coupler or a preformed dye diffuses into an image-receiving layer.

In one conventional process, use is made of the fact that the dye formed during chromogenic development is resistant to diffusion, while the color-forming coupler from which it is formed and which in principle is capable of diffusion by virtue of its average molecular weight, is so incorporated in the photosensitive layer in the form of "oil packs," i.e. dissolved in droplets of a high-boiling low molecular weight organic solvent substantially insoluble in water, as to be resistant to diffusion. This process is described, for example, in German Pat. Nos. 1,150,278 and 1,272,716. Unfortunately, due both to the nature of the hydrophilizing groups required for diffusion and to the nature of the developers used, it is necessary in this process to operate at an extremely high pH value in order to achieve diffusion of the couplers. This process gives azomethine dyes which have their conventional disadvantages, for example limited stability and inadequate resistance to light.

In another conventional process, use is made of so-called dye developers, i.e. compounds which contain in the same molecule a dye radical and a group which is capable of developing silver halide. This process is described, for example, in German Pat. No. 1,196,075. Unfortunately, extremely complicated materials are required for carrying out this process. In addition, it is necessary in this case too to operate at an extremely high pH value due to the nature of the diffusion-promoting hydrophilizing groups, usually phenolic hydroxyl groups.

In a third color photographic diffusion process which is described, for example, in German Pat. No. 1,095,115 or in the corresponding U.S. Pat. No. 3,227,550, nondiffusing couplers are used in which case development with color-forming developers is accompanied by the cleavage of a bond which through a linking members, links the per se diffusion-resistant coupler radical with a per se diffusible dye radical or second coupler radical, or a radical rendering the molecule resistant to diffusion with the per se diffusible coupler radical. Reference is made in the aforementioned patent specification to the couplers commonly used in photography such as 5-pyrazolone derivatives, phenol and α -naphthol derivatives and open-chain ketomethylene compounds. In the case of the 5-pyrazolone compounds, the coupling position of the coupler molecule is the carbon atom in the 4-position, in the case of the phenols and α -naphthols, similarly, the coupling position is

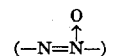
the carbon atom in the 4-position and in the case of the open-chain ketomethylene couplers the coupling position is the carbon atom of the methylene group in the group $-\text{CO}-\text{CH}_2-\text{CO}-$.

During the coupling reaction of the couplers with oxidized color-forming developers the substituent in the coupling position is split off, resulting in the formation either of a diffusing azomethine dye or even, where the coupler portion is diffusion resistance, of a diffusing dye which may be of another type, depending on the way in which the process is carried out. The diffusible dyes formed diffuse out of the photosensitive layer into an image-receiving layer being in intimate contact with the photosensitive layer whereupon the dyes are anchored in the receiving layer by mordanting.

The individual steps of this process have been known for some considerable time. For example, the process in which dyes diffuse to form an image is based on the Technicolor process. Reference is also made in this connection to Bela Gaspar's imbibition process. It is also known that the principle of splitting off radicals situated in the coupling position of color-forming couplers can be used to form a color image. This can be seen, for example, from U.S. Pat. Nos. 2,435,616; 2,453,661 and 2,455,169.

Although by combination of these individual steps an extremely interesting and technically advanced dye diffusion transfer process may be obtained, this process is nevertheless attended by certain disadvantages. For example, the diffusing dyes are usually azomethine dyes to which reference has already been made, and accordingly show only a moderate stability and fastness to light. However, other serious disadvantages arise where dyes which can belong to a different class of dyes and which hence can be more resistant to light, are split off from the coupling position of diffusion-resistant couplers in this process.

That portion of molecule to be split off in coupling through oxidation is attached to the "coupling position" through a connecting or linkage radical such as azo ($-\text{N}=\text{N}-$), azoxy

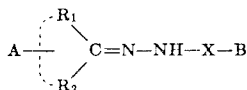


mercury ($-\text{Hg}-$), oxy ($-\text{O}-$), alkylidene (includes both $\text{CH}-$ and $=\text{CH}-$), thio ($-\text{S}-$), or dithio ($-\text{S}-\text{S}-$). Unfortunately, not all the proposed groups have proved to be of equal advantage. For example, some of them, for example the groups $-\text{Hg}-$, $-\text{O}-$ and $\text{CH}-$, are not suitable for use in practice because they are split off much too slowly. In addition, it is only the azo bond that is specifically disclosed in the corresponding patent literature, for example in U.S. Pat. No. 3,227,550, as the cleavable bond between light-fast dye and diffusion resistant coupler portion. If, however, the azo group is selected as the bridge member, the reaction with oxidized color-forming developer is accompanied in the known manner by the formation of nitrogen which partly escapes from the layer in the form of microscopic bubbles and interrupts the necessary contact between the dye-giving layer and the image-receiving layer. This is particularly the case where heating is used to accelerate the process.

Unfortunately, the thioether group which is as already known readily split off from the coupling position of couplers during the reaction with oxidized color-forming developer, can only be used with certain disadvantages as the bridge member between the diffusion-resistant coupler and the diffusible dye radical in this dye-diffusion process. The reason for this is that it is known that mercaptans which are, of course, formed during this reaction either react very readily with silver halide to form silver mercaptides through a chemical reaction or are retained by the silver halide through adsorption. Use is made of this fact, for example, in cases where DIR couplers (development inhibitor releasing couplers) are used. Unfortunately, these properties represent an obstacle to the need for quick and quantitative diffusion of the dyes liberated.

The object of the present invention is to provide both a simple dye-diffusion process and a photographic material suitable for use in this process which does not have any of the disadvantages affecting the processes referred to above.

A color photographic diffusion transfer process has now been found in which at least one silver halide emulsion layer of a photosensitive material is exposed and developed to form a color image and in which a dye which has been rendered diffusible through development is transferred imagewise at least in part to a receiving layer, and which is characterized by the fact that a compound of the following formula is incorporated in diffusion-fast form in the silver halide emulsion layer or in a layer adjacent thereto which compound is called "dye-giving compound" hereinafter:



in which

R₁ represents hydrogen, an alkyl group with up to 20 carbon atoms and preferably with one to five carbon atoms, an aralkyl group for example benzyl, an aryl group, for example phenyl, an amino group substituted by alkyl or aryl, for example phenyl, in which case two alkyl groups on the nitrogen atom can be closed together to form a ring;

R₂ represents an alkyl group with up to 20 carbon atoms, an aralkyl group, for example benzyl, an aryl group, for example phenyl, an acyl group derived from aliphatic carboxylic acids with up to 20 carbon atoms or aromatic carboxylic acids, for example benzoyl, an amino group substituted by alkyl or aryl, for example phenyl, in which case two alkyl groups on the nitrogen can be closed together to form a ring; or

R₁ and R₂ together represent the ring members required to complete a preferably 5- or 6-membered isocyclic or heterocyclic group with an optionally anellated benzene ring; at least one of the radicals R₁ and R₂ contains 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 is a dye radical; or

A represents a dye radical either on its own or together with R₂; and

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

In the present context, radicals rendering the dye-giving compounds resistant to diffusion include radicals of the kind which enable the compounds according to the invention to be so incorporated in the hydrophilic colloids conventionally used in color photographic materials, as to be resistant to diffusion. It is preferred to use for this purpose organic radicals which may generally contain linear or branched aliphatic groups and optionally also isocyclic or heterocyclic aromatic groups. The aliphatic portion of these radicals generally contains from eight to 20 carbon atoms. These radicals are attached to the remaining portion of the molecule either directly or indirectly, for example, through one of the following groups:

—CONH—, —SO₂NH—, —CO—, —SO₂—, —NR— in which R represents hydrogen or alkyl, —O— or —S—.

In addition, the radical rendering the dye-giving compounds resistant to diffusion may also contain water-solubilizing groups such as, for example, sulfo groups or carboxyl groups which may also be present in the anionic form. Since the diffusion properties are governed by the molecular size of the overall compound used, it is even sufficient in certain cases,

for example when the size of the total molecule used is great enough, to use shorter-chain radicals as the radicals rendering the dye-giving compound resistant to diffusion.

Basically, the radicals of dyes of all classes may be used as the dye radicals providing they are sufficiently diffusible after cleavage to be able to diffuse through the layers of the photosensitive material into the image-receiving layer. On account of this requirement, the dye radicals are preferably provided with at least one but generally with a plurality of water-solubilizing groups. Suitable water-solubilizing groups include inter alia carboxyl groups, sulfo groups, hydroxyl groups or hydroxy alkyl groups. The following are mentioned as examples of dyes particularly suitable for use in the process according to the invention: azo dyes, anthraquinone dyes, phthalocyanine dyes, indigo dyes and triphenyl methane dyes.

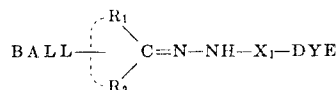
The process according to the invention is distinguished from the processes referred to in the foregoing in regard inter alia to the compounds used which do not contain any of the coupler radicals commonly used in conventional color photography.

Another feature which distinguishes the process according to the invention from conventional processes is the relatively wide range of suitable developer substances because the nuance of the dyes transferred is not determined by the chemical structure of the developer molecule.

The dyes split off from the dye-giving compounds according to the invention during the reaction with developer oxidation products must be sufficiently hydrophilic to enable quick and substantially quantitative diffusion to be obtained. The hydrophilic properties are usually imparted by sulfo groups or carboxyl groups. It is known from coupler chemistry that it is necessary to achieve a balance between the size of the radicals rendering the dye-giving compounds resistant to diffusion and the number of solubilizing groups to ensure on the one hand adequate resistance to diffusion and on the other hand adequate solubility in aqueous-alkaline media. Thus, the greater the number of solubilizing groups, the lower is the resistance to diffusion. The larger the dye molecular split off, the greater the number of solubilizing groups required for diffusion.

Two requirements have to be satisfied in the dye diffusion transfer process according to the invention. The dye-giving compounds according to the invention have to be embedded in the photosensitive layer or in a layer adjacent thereto so as to be completely resistant to diffusion, and the dyes liberated during the reaction with the developer oxidation products have to be highly soluble in the reaction media and diffusible. The dye radical of the dye-giving compound is usually very large so that the dye split off should be as hydrophilic as possible, i.e. should contain as many solubilizing groups as possible, in order to obtain the necessary diffusion rate. On the other hand, the resistance to diffusion of the dye-giving compounds used in accordance with the invention has to meet the same requirements as in conventional chromogenic processes, that is to say these compounds should contain as few solubilizing groups as possible so that they are optimally resistant to diffusion. Accordingly, it is desirable for solubilizing groups which remain connected with the dye molecule and impart to it a certain additional capability of diffusion, to be formed during the cleavage reaction.

In one particularly preferred embodiment of the process according to the invention, therefore, compounds so incorporated as to be resistant to diffusion are used, corresponding to the general formula:



in which

R₁ and R₂ are as defined above; at least one of the radicals R₁ and R₂ contains the group BALL;

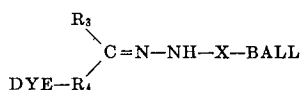
X_1 represents a sulfonyl group or a carbonyl group;
BALL represents a ballasting photographically inert radical rendering the dye-giving compound resistant to diffusion; and

DYE is a dye radical.

In this embodiment, both the dye radical and the radical rendering the dye-giving compound resistant to diffusion contain solubilizing groups, preferably sulfo groups. Thus, by selecting both the number and the position of the solubilizing groups, it is possible to adapt the diffusion resistance of the dye-giving compound and the diffusibility and the ability of the diffusing dyes to be absorbed by the mordants of the receiving layer, to the particular practical requirements. Thus, it has proved to be of particular advantage in this embodiment, for example, when X_1 represents a sulfonyl group, that it is also possible to use dye-giving compounds which do not contain any solubilizing groups or fewer than required for diffusion. An extremely high resistance to diffusion is obtained in this way. Nevertheless, the dye split off is able to diffuse because an additional water-solubilizing group which remains in the dye molecule is formed from the sulfonyl group during cleavage by the developer oxidation product. In this way, not only are the dyes split off capable of diffusion, but also the starting compounds are highly insoluble in the photosensitive layer and hence resistant to diffusion.

In this embodiment, R_1 and R_2 together preferably represent the ring members required to complete a heterocyclic group with a 5- or 6-membered heterocyclic ring, for example with the oxazoline, thiazoline, imidazoline, pyrrolidine, pyrroline, 1,2-dihydropyridine, 1,4-dihydropyridine, thiadiazoline, pyrazoline or triazoline ring which rings can have benzene rings condensed thereto. The heterocyclic group advantageously contains at least one polar water-solubilizing group, for example a sulfo group or carboxyl group, either directly or by way of a substituent, for example by way of a short-chain alkyl group. Nevertheless, other combinations, for example $R_1 = H$ and $R_2 = \text{aryl}$, are also possible. Dye preferably represents a light-resistant dye radical, for example an azo dye radical, an anthraquinone dye radical or a phthalocyanine dye radical.

In another embodiment of the process according to the invention, a compound so incorporated as to be resistant to diffusion is used, corresponding to the formula:



in which:

R_3 represents hydrogen, an alkyl group, preferably with one to five carbon atoms, for example methyl, ethyl, or propyl, an aralkyl group, for example benzyl, or an aryl group, for example phenyl;

R_4 represents an aryl group, for example a phenyl group which can 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; and

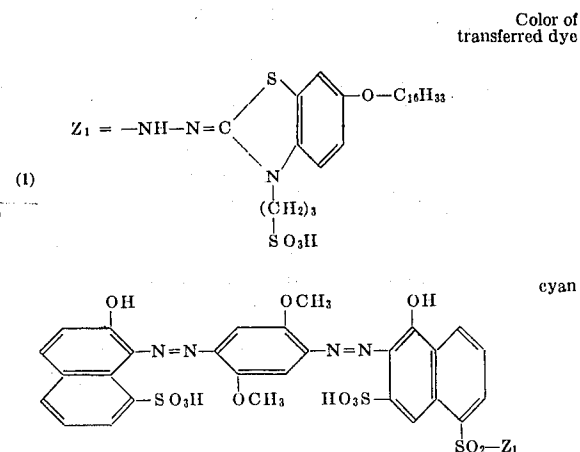
DYE represents a dye radical either on its own or together with R_4 .

In this case, R_4 preferably represents an aryl group, for example a phenyl group, to which a dye radical is attached either directly or indirectly, or which itself represent part of the chromophoric system of such a dye radical. In this latter case, the aryl group can be linked in any position, for example in the o-, m or p-position, through an azo group to an isocyclic or heterocyclic aromatic group, for example to an aryl group or to a 5-pyrazolone group, and together with this group can thus form a dye.

The dye-giving compounds originally fixedly incorporated in the layer are split during the reaction with developer oxidation products, as a result of which the dyes are released from their anchorage. Since they generally contain one or even several solubilizing groups, they are able to diffuse into the image-receiving layer which is in intimate contact with the photosensitive layers at least during the development and wherein they are fixed by means of the dye mordant. The radical rendering the dye-giving compound resistant to diffusion remains behind in the emulsion layer.

Since no dye is reformed in any of the aforementioned embodiments and since in addition no dye is destroyed as for example in the azo dye bleaching process, it is a unique feature of the dye diffusion transfer process according to the invention that, following dye transfer, the two layers, namely the emulsion layer and the image-receiving layer, have the same color but in opposite gradation.

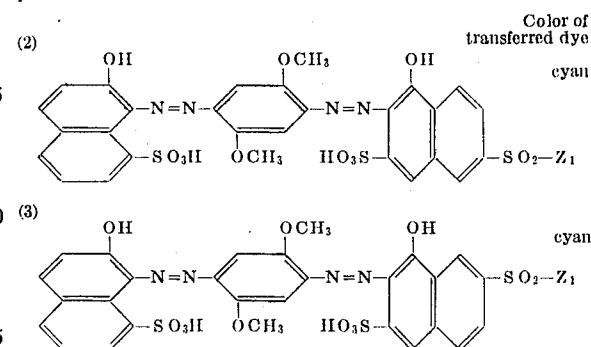
The following are examples of suitable dye-giving compounds:



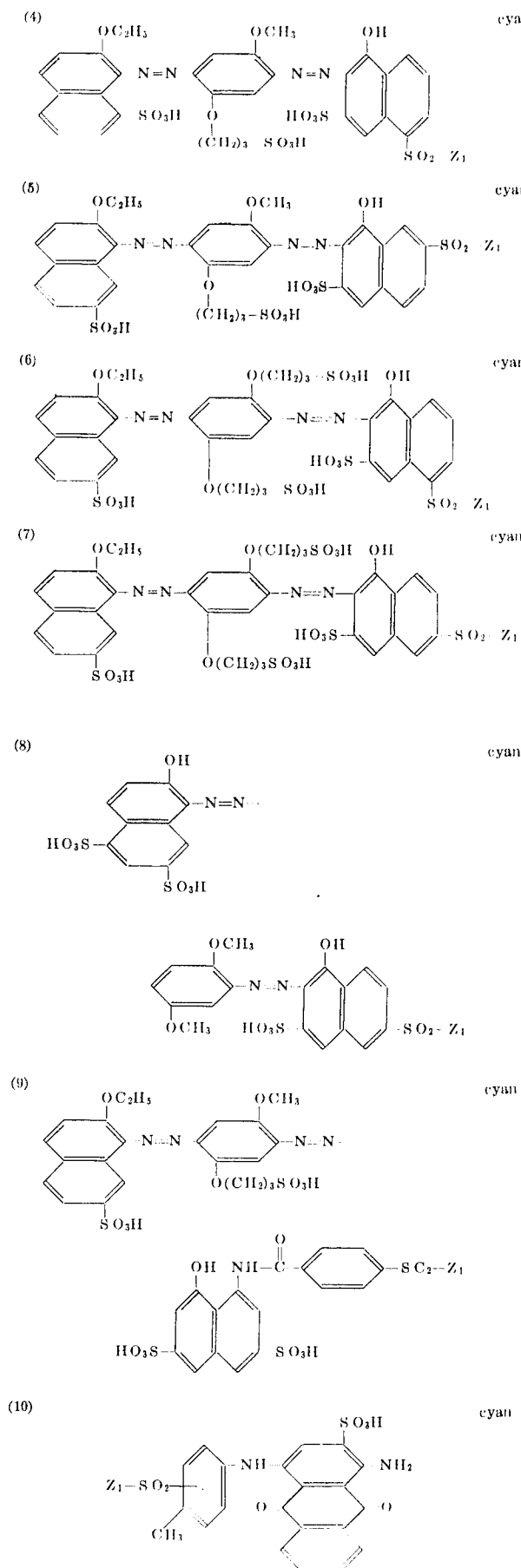
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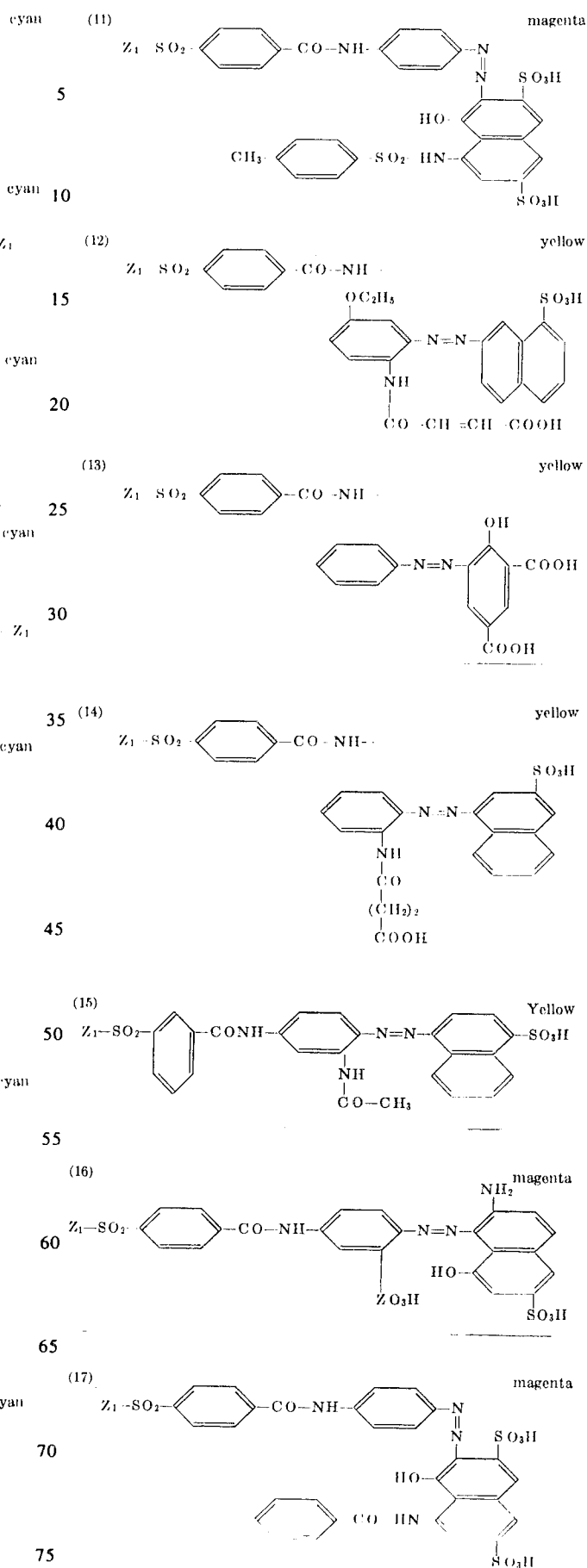
The following are examples of suitable dye-giving compounds:



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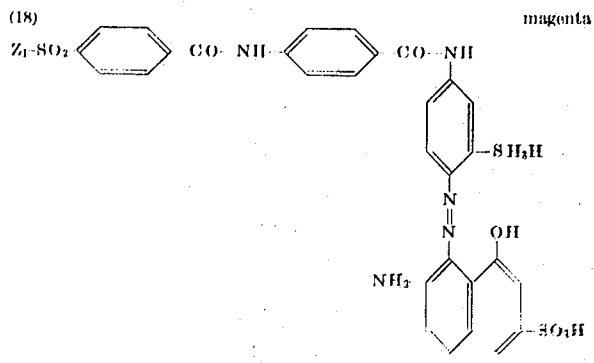
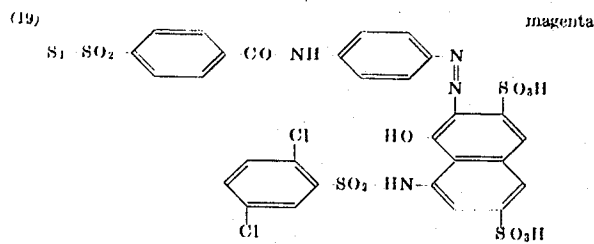
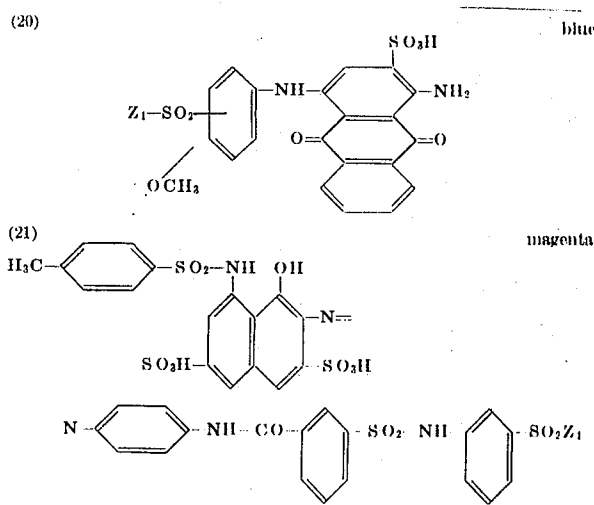
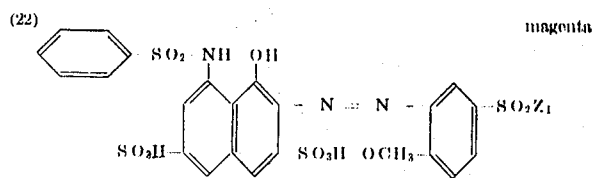
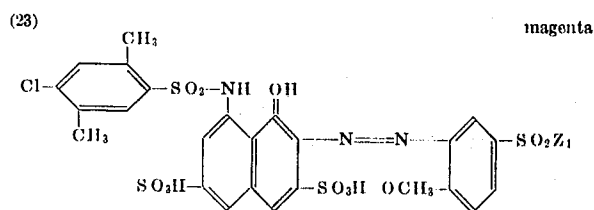
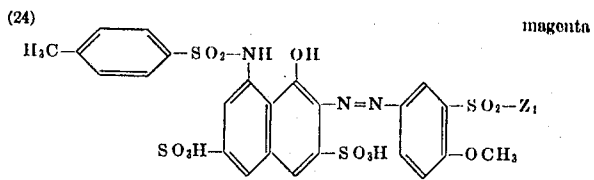
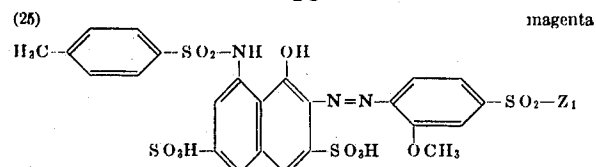
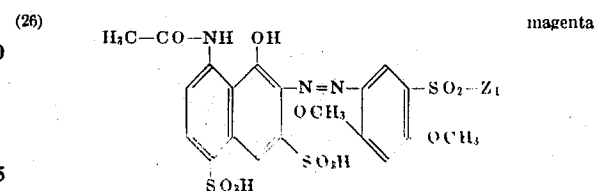
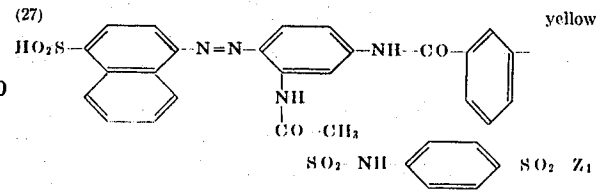
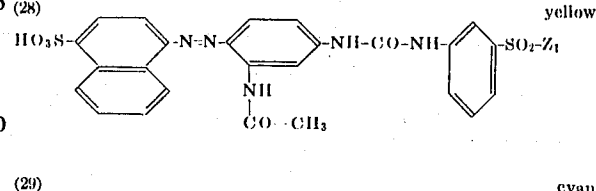
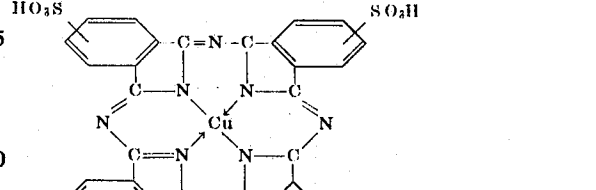
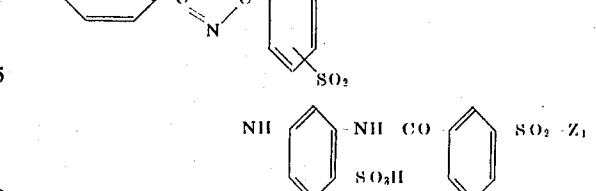
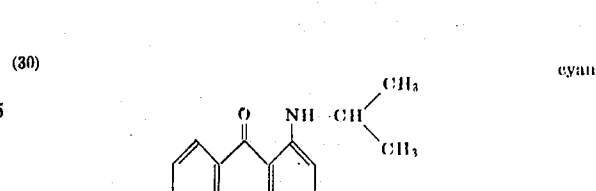
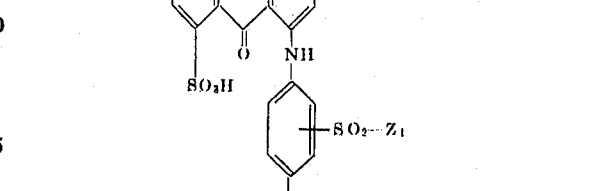
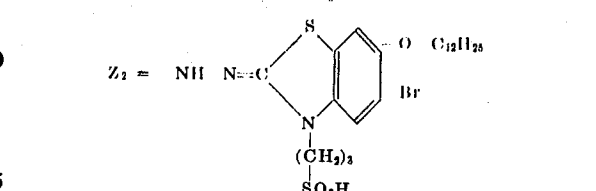


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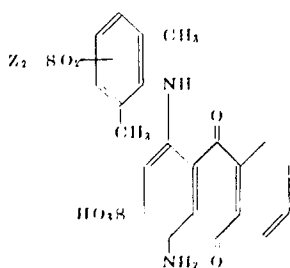
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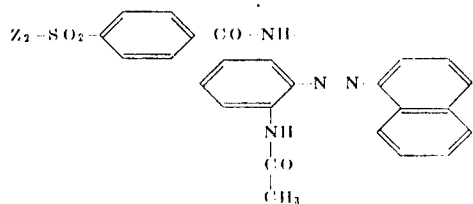


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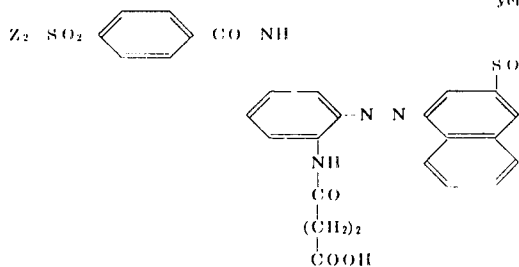
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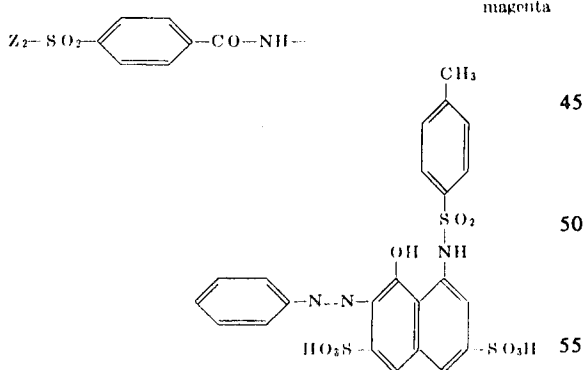
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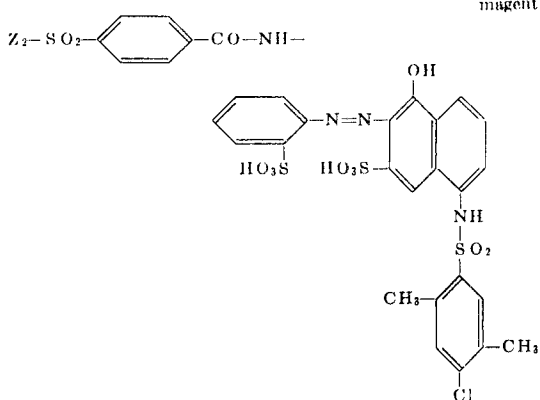
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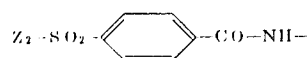
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12

cyan

(36)



magenta

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yellow

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yellow

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magenta

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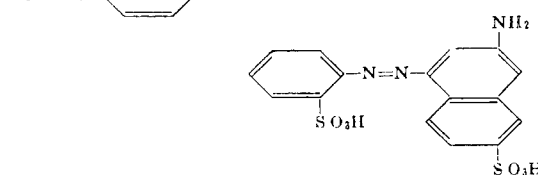
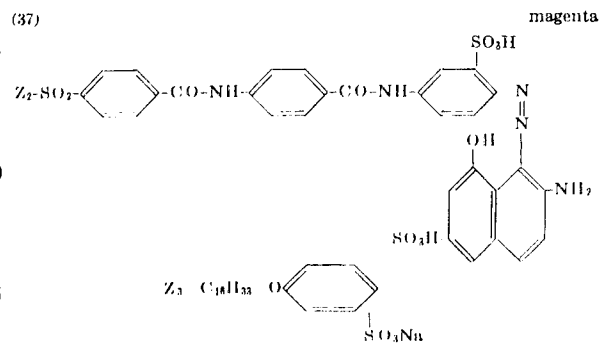
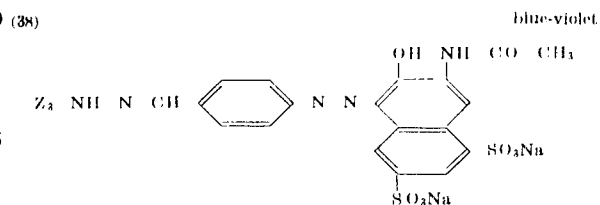
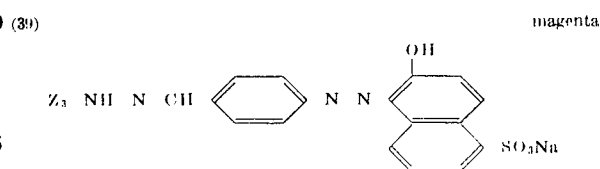
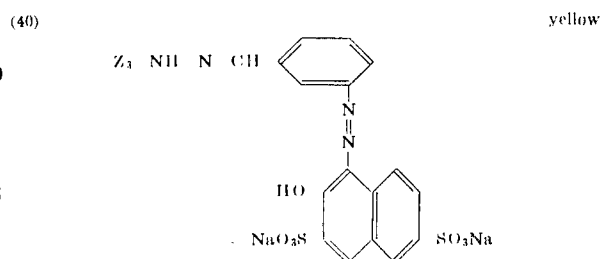
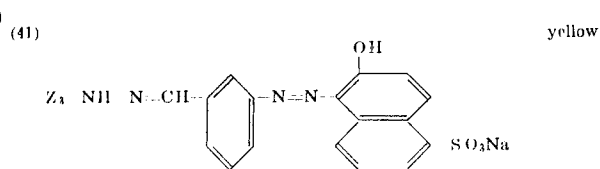
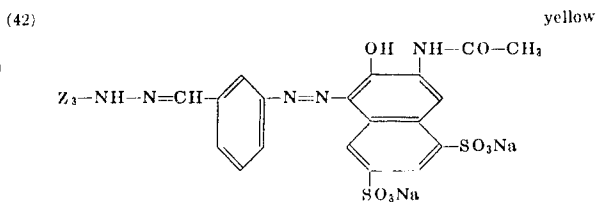
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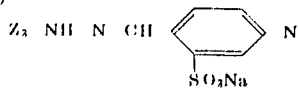
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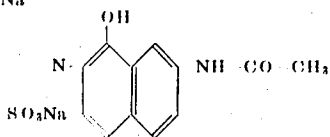
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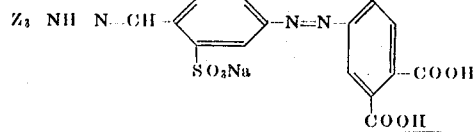


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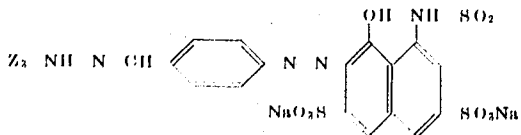


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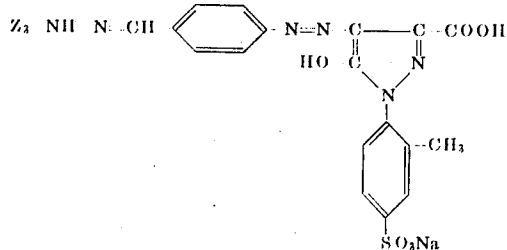
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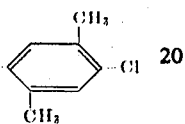
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10 (51)



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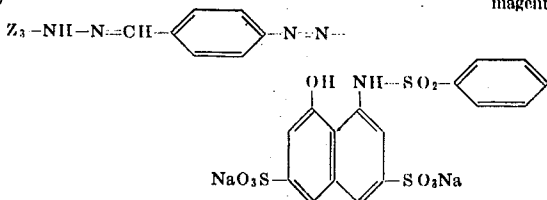
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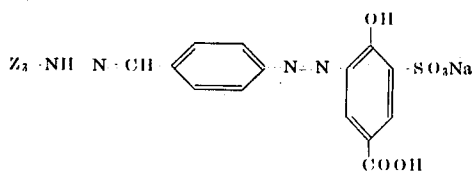
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(45)



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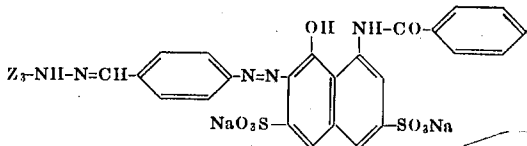


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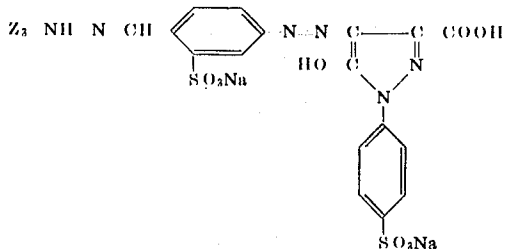
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(46)



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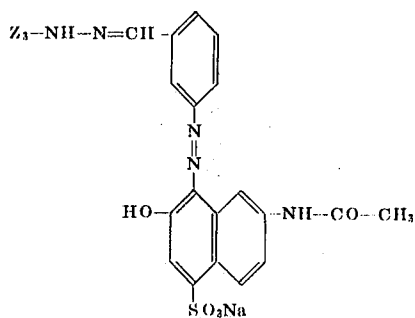
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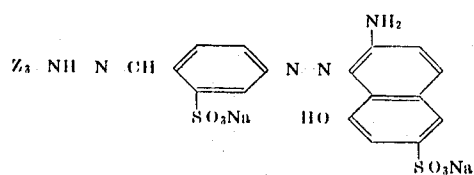
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red

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(54)



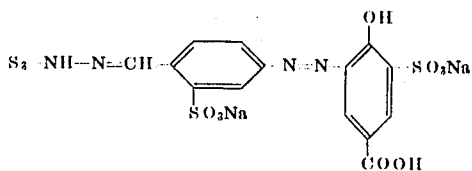
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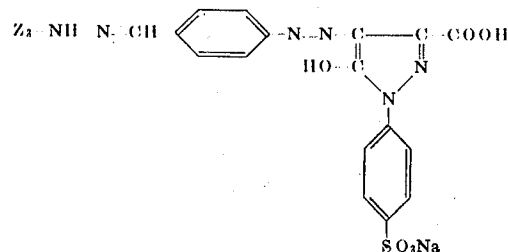
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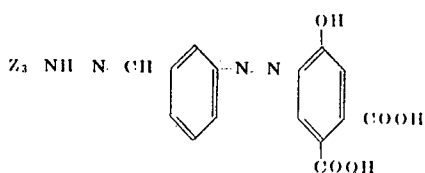
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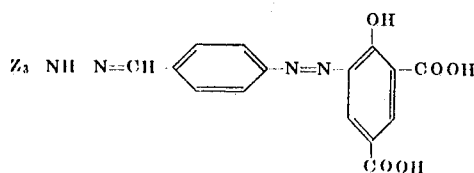
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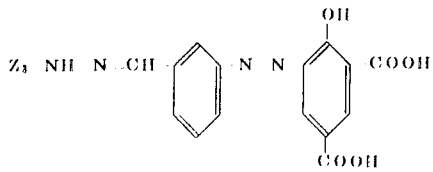


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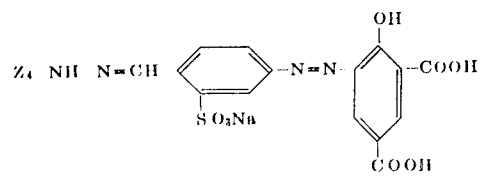
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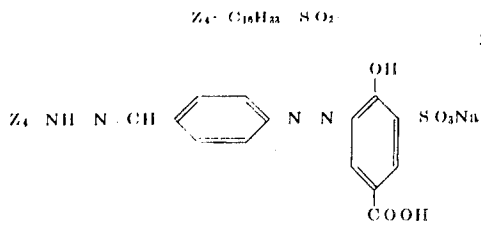
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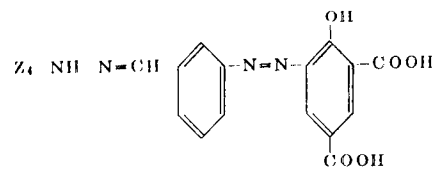
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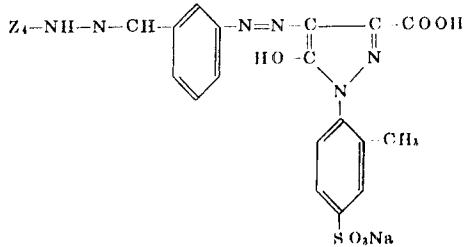
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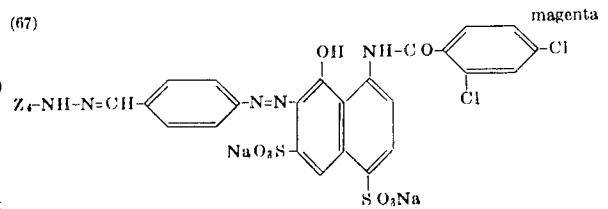
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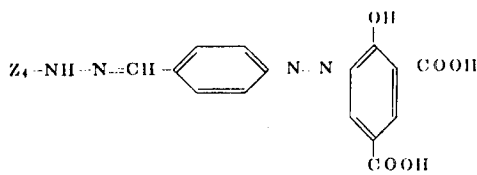
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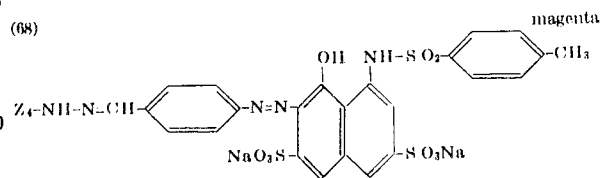
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yellow (68)

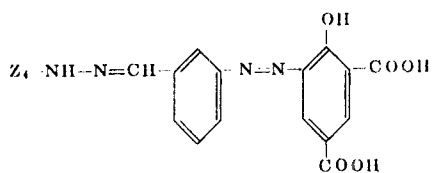
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magenta

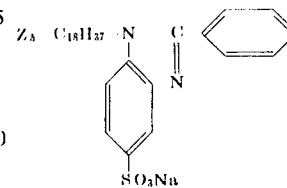
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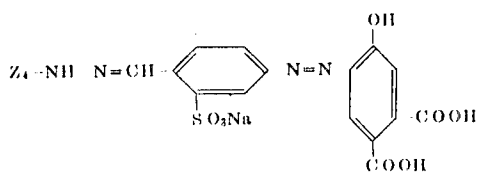
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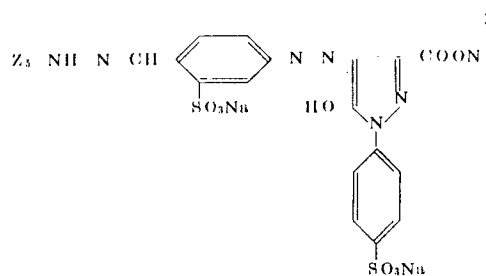
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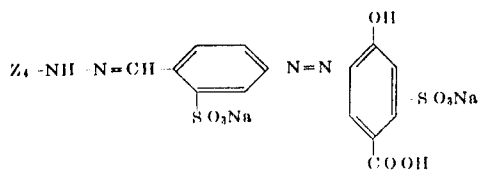
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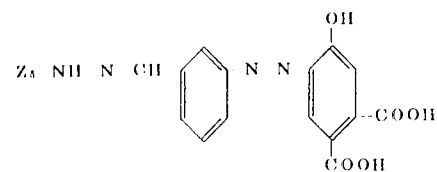
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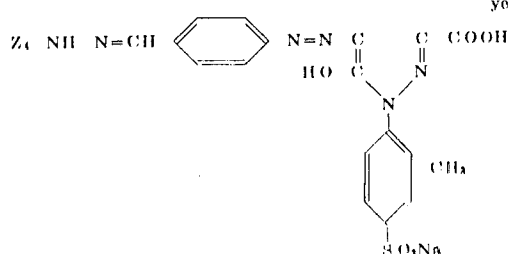
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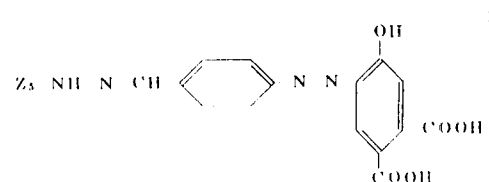
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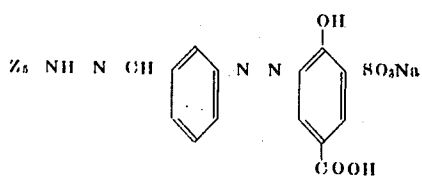
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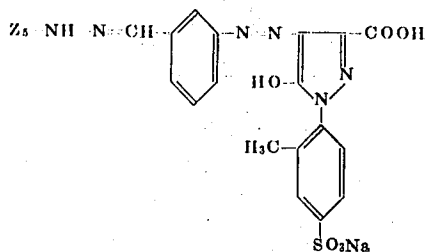
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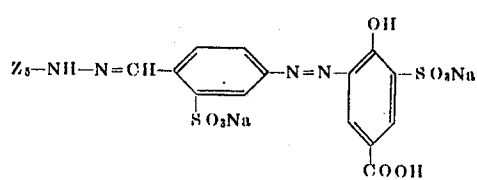
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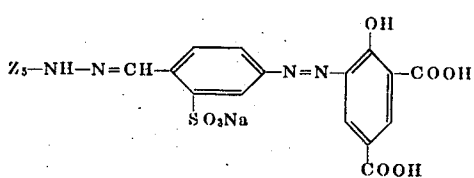
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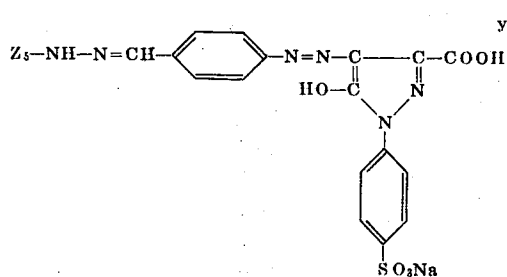
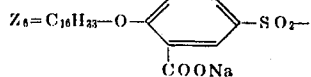
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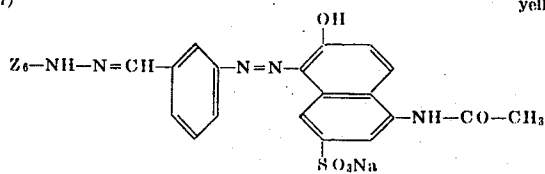
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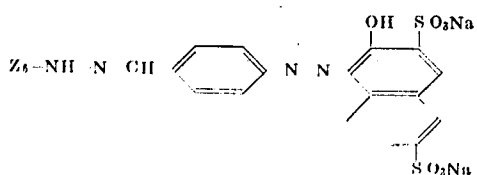
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(77)

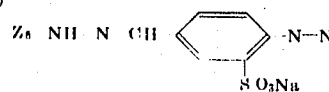


(78)



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(79)



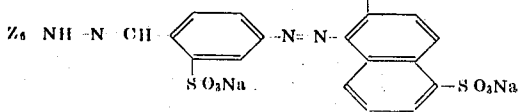
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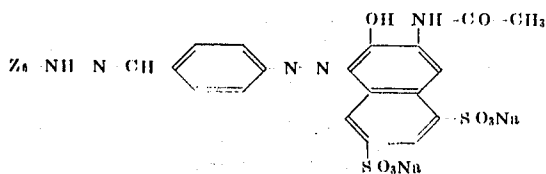
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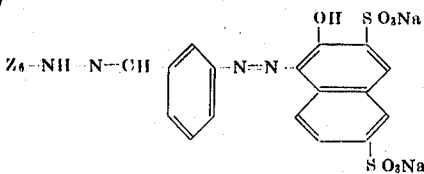
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yellow

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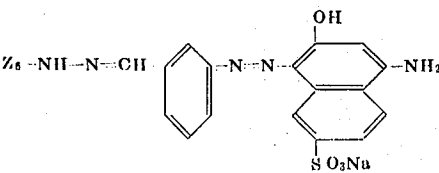


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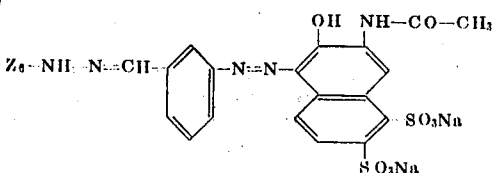
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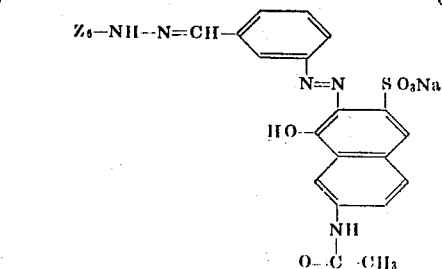


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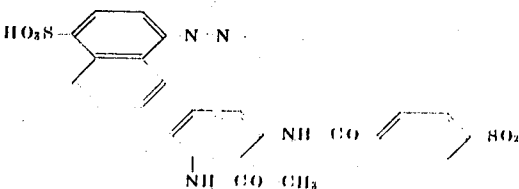
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65

magenta

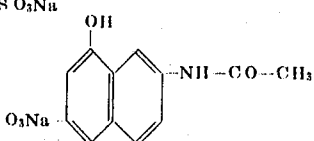
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75

18

magenta



red

magenta

yellow

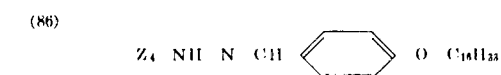
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yellow

orange-yellow

19

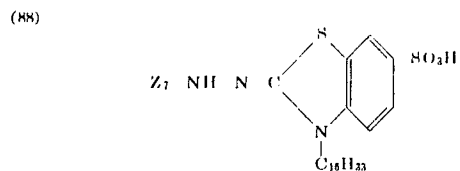
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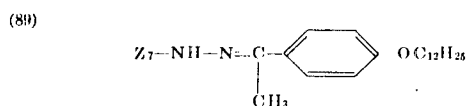
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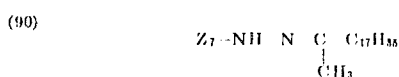
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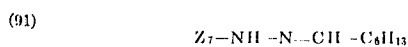
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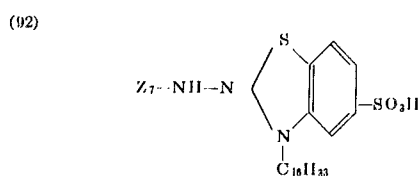
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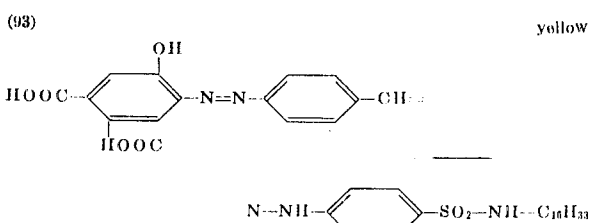
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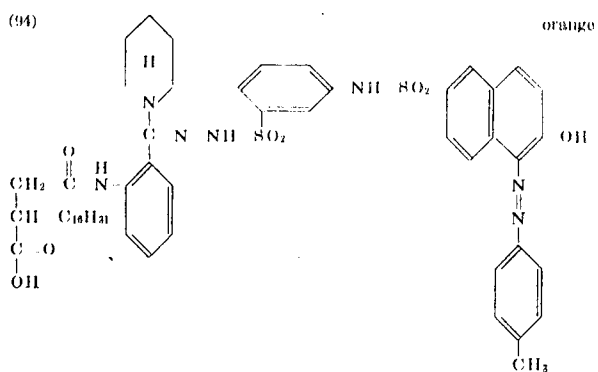
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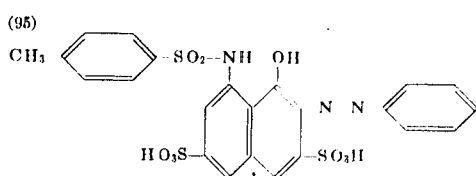
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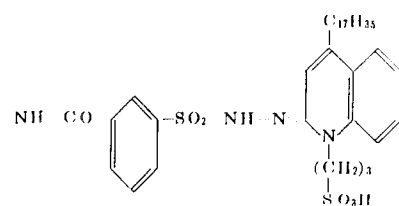
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orange



magenta



5

10

(96)

yellow

15

(97)

yellow

20

25

(98)

yellow

35

40

(99)

45

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55

(100)

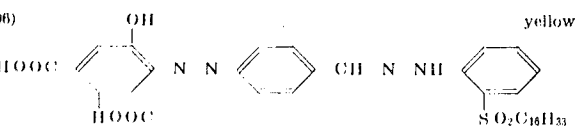
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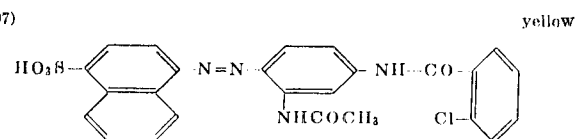
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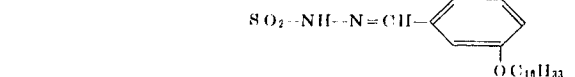
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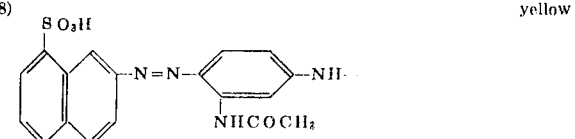
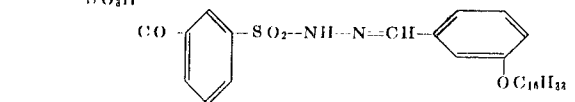
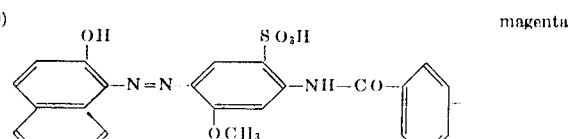
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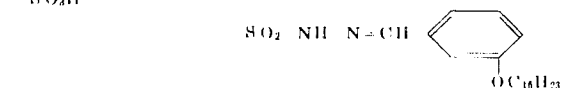
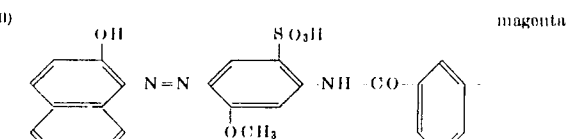
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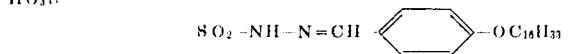
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magenta

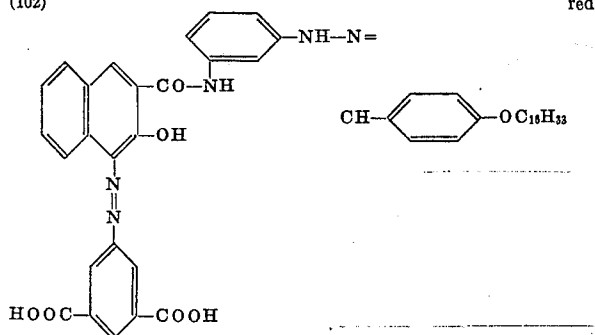


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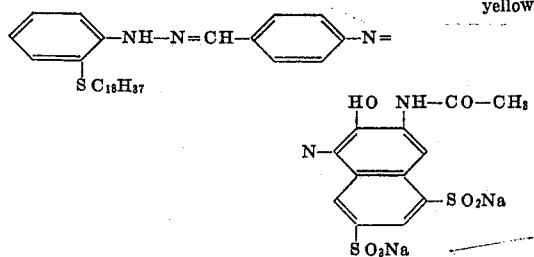
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(102)



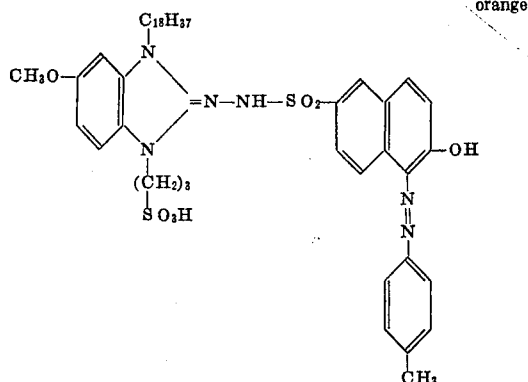
red

(103)



yellow

(104)



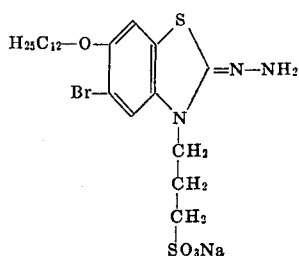
orange

The dye-giving compounds according to the invention can be prepared by methods known from the literature. For example, the hydrazones of the carbonyl compounds, for example benzthiazolone hydrazones or benzaldehyde hydrazones, can be reacted with sulfonic acid halides such as sulfonic acid chlorides or sulfonic acid fluorides. However, the reverse procedure is also possible, in which case the carbonyl compounds are used as the starting materials and are reacted with hydrazines or carboxylic acid hydrazides or sulphydrazides. In connection with the synthesis of the compounds according to the invention, reference is made to S. Hunig, *Angewandte Chemie*, 80, 343 (1968), and other literature references quoted therein.

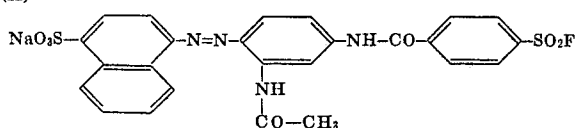
The synthesis of a few compounds is described in the following by way of illustration:

Compound 32 (sodium salt):

(I)



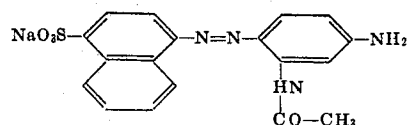
(II)



5.7 Parts of the hydrazone of formula I are dissolved at 50° C. in 200 parts of water and 40 parts of pyridine. 5.9 Parts of the dye of formula II are then introduced into the resulting solution over a period of 30 minutes, after which the mixture is heated to 90° C. and retained at this temperature for 40 minutes. After cooling, the mixture is clarified, 80 parts of methanol are added followed by the introduction of 21.5 parts of sodium chloride. The mixture is stirred for 15 minutes, the precipitate filtered under suction and then poured with stirring into 100 parts of acetone. 6.7 Parts of the sodium salt of the compound 32 are obtained after the residue has been suction-filtered and dried.

Compound I is prepared by methods known from the literature. The dye of formula II is obtained as follows:

6.5 Parts of the dye of formula III:



III

prepared by the methods normally employed in azo chemistry, are dissolved in 150 parts of water. A solution of 3.65 parts of 4-fluorosulfonyl benzoyl chloride (whose preparation is described in *J. Org. Chem.* 30, page 1498 (1965)) in 30 parts of acetone is then added dropwise over a period of 30 minutes, during which a pH value of from 6.5 to 7 is maintained by the simultaneous dropwise addition of a 10 percent soda solution. The mixture is stirred for 1 hour at pH 8, after which 20 parts of sodium chloride are added. It is then heated to 70° C. and, after cooling, the precipitate is filtered under suction. The residue is triturated with acetone and filtered. 9 Parts of the dye of formula II are obtained after drying.

Compound 87 (sodium salt)

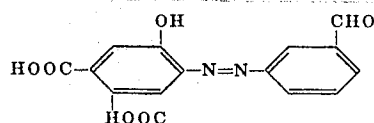
2.91 g. (0.005 mol) of the sulphydrazide prepared from the aforementioned compound II and 3.81 g. (0.006 mol) of m-hexadecyloxy benzaldehyde are heated for 3 hours to 55° to 60° C. in 50 ml. of anhydrous pyridine and 50 ml. of anhydrous dimethyl formamide, and after cooling, precipitated with 600 ml. of a 20 percent NaCl solution. The precipitate is filtered under suction, washed with 20 ml. of water and dried with acetone. The excess aldehyde is removed by washing with ether.

Yield: 3.96 g., corresponding to 86 percent of the theoretical yield.

Compound 66

7.54 g. (0.024 mol) of the azo dye aldehyde of formula IV obtained from m-aminobenzaldehyde by diazotization and coupling with 4-hydroxy phthalic acid

IV



4.92 g. (0.06 mol) of sodium acetate and 6.4 g. (0.02 mol) of cetyl sulphydrazide are suspended in 100 ml. of alcohol/water (1:1), and the resulting suspension heated for 2 hours to 60° C. It is then cooled to 15° C., filtered under suction, washed with acetone and ether and then dried.

Yield: 9.3 g. corresponding to 76.7 percent of the theoretical yield.

Compound 49

7.54 g. (0.024 mol) of the aforementioned compound IV 4.92 g. (0.06 mol) of sodium acetate, and 8.56 g. (0.02 mol) of p-hexadecyloxy-o-sulphophenyl-hydrazine are heated for 1 hour to 50° C. in 100 ml. of pyridine/water (1:1), cooled and 30 g. of ice added. The excess pyridine is buffered to a pH of 6 by the addition of 6 N hydrochloric acid, as a result of which the hydrazone is precipitated. It is suction filtered and dried. The almost dry product is triturated with acetone, filtered under suction and washed with ether.

Yield: 10.0 g. corresponding to 67.1 percent of the theoretical yield.

The materials required for carrying out the process according to the invention basically consist of two elements, namely a photosensitive material containing at least one silver halide emulsion layer and at least one of the dye-giving compounds according to the invention, and a nonphotosensitive image-receiving material which contains a dye mordant and which is intended to absorb the diffusing dye.

Conventional silver halide emulsions are suitable for the purposes of the invention. These emulsions may be based on silver halide, silver chloride, silver bromide or mixtures thereof, optionally with a small silver iodide content of up to 10 mol percent.

Gelatin is preferably used as a binder for the photographic layers. However, it can be replaced at least in part by other natural or synthetic binders. Suitable natural binders include, for example, alginic acid, and its derivatives such as its salts, esters or amides, cellulose derivatives such as carboxymethyl cellulose, alkyl celluloses such as hydroxy ethyl cellulose, starch or its derivatives such as its ethers or esters or caragenates. Suitable synthetic binders include polyvinyl alcohol, partially hydrolyzed polyvinyl acetate and polyvinyl pyrrolidone.

The emulsions can also be chemically sensitized, for example by the addition during chemical ripening of sulfur-containing compounds such as, for example, allyl isothiocyanate, allyl thiourea and sodium thiosulfate. Other suitable chemical sensitizers include reducing agents, for example the tin compounds described in Belgian Pat. Nos. 493,464 or 568,687, also polyamines such as diethylene-triamine, or aminomethane-sulfinic acid derivatives, for example those of the kind described in Belgian Pat. No. 547,323.

Other suitable chemical sensitizers include noble metals or noble metal compounds such as gold, platinum, palladium, iridium, ruthenium or rhodium. This method of chemical sensitization is described in the article by R. Koslowsky, *Z. Wiss. Phot.* 46, 65-72 (1951).

The emulsions can also be sensitized with polyalkylene oxide derivatives, for example with polyethylene oxide with an average molecular weight of from 1,000 to 20,000, also with condensation products of alkylene oxides and aliphatic alcohols, glycols, cyclic dehydration products of hexitols, with alkyl-substituted phenols, aliphatic carboxylic acids aliphatic amines, aliphatic diamines and amides. The condensation products have a molecular weight of at least 700 and preferably in an excess of 1,000. In order to obtain special effects, these sensitizers can, of course, be used in combination as described in Belgian Pat. No. 537,278 and in British Pat. No. 727,982.

The emulsions can also be spectrally sensitized, for example with the usual monomethine or polymethine dyes such as cyanines, hemicyanines, streptocyanines, merocyanines, oxonoles, hemioxonoles, styryl dyes or other methine dyes which also can contain three or more nuclei, for example, rhodacyanines or neocyanines. Sensitizers of this kind are described in the book by F. M. Hamer "The Cyanine Dyes and Related Compounds" (1967), Interscience Publishers, John Wiley and Sons.

The emulsions can contain the usual stabilizers, for example homopolar or saltlike compounds of mercury with aromatic or heterocyclic rings, such as mercaptotriazoles, simple mercury salts, sulfonium mercury double salts and other mercury compounds. Other suitable stabilizers include azaindenes, preferably tetra- or penta-azaindenes, especially those that are substituted by hydroxyl or amino groups. Compounds of this kind are described in the article by Birr, *Z. Wiss. Phot.* 47, 2-58 (1952). Other suitable stabilizers include inter alia heterocyclic mercapto compounds, for example phenyl mercapto tetrazole, quaternary benzothiazole derivatives and benzotriazole.

The emulsions can be hardened in the conventional manner, for example with formaldehyde or with halogen-substituted aldehydes containing a carboxyl group, such as mucobromid acid, diketones, methane sulfonic acid esters and dialdehydes.

The emulsions may be either conventional negative emulsions or even direct positive emulsions, for example those of the kind which have a high sensitivity inside the silver halide grains, or even emulsions which function in accordance with the principle of solarization. The choice of the emulsions is governed by the purpose for which it is intended to use the end product. If, for example, it is intended to produce a positive image from a positive original, for example from a color transparency, direct positive emulsions would preferably be used. It is, of course, also possible to process a negative emulsion in a reverse development to form a corresponding positive image.

In cases where colored images are required, it is possible to use a material in which the photosensitive material contains only one photosensitive layer and, for example, only one of the dye-giving compounds according to the invention. In general, however, a photosensitive color photographic multilayer material with at least three separate silver halide emulsion layers of which, for example, one is sensitive to red light, another to green light and a third to blue light, will be used for the production of multicolor images. Each of the aforementioned photosensitive layers is in intimate contact with one of the dye-giving compounds according to the invention.

The intimate contact between the dye-giving compound and the silver halide required to obtain the desired effect can be established by introducing the dye-giving compounds from aqueous-alkaline solutions into the silver halide emulsion layers utilizing the water-solubilizing groups present. However, the diffusion-resistant compounds can also be introduced into the layers by any one of the conventional emulsification processes. These processes are described, for example, in British Pat. Nos. 791,219 and 1,099,414 to 1,099,417. In another embodiment, it may be desirable, for example, to incorporate the dye-giving compounds together with silver halide and optionally developer substances in the layer in the form of so-called microcapsules, in which case two or more differently sensitized photosensitive silver halide emulsions and the corresponding diffusion-resistant compounds can also be combined in a single layer on the lines of so-called mixed-grain emulsions as described, for example, in U.S. Pat. No. 2,698,794. The diffusion-resistant dyes can be incorporated either in a photosensitive layer itself or in an adjacent layer. For example, the red-sensitive layer is associated with a cyan dye, the green-sensitive layer with a magenta dye and the blue-sensitive layer with a yellow dye. In addition, the multilayer material can contain intermediate layers in which there are incorporated other substances such as, for example, filter dyes, white couplers or antioxidants in order to limit the activity of the developer oxidation products in each case to the photosensitive layer, wherein they are formed and the layers wherein the oxidation products are desired to become active. As already mentioned, the layers of the photosensitive material can also contain as a further additive developer substances, for example conventional color-forming developers of the p-phenylene diamine type, and also other developers, for example hydroquinone catechol, N-methyl aminophenol or phenidone. The developers may be embedded in the layer in the form of their free molecules or in the form of their salts. Since they should only exert their effect during the initial stages of the actual development process, a diffusion-resistant anchorage of the developer substances in the layers should be obtained if possible. Thus, the developers may be introduced into the layer, for example, again in the form of the aforementioned packs. Another possibility is to use developing agent precursors or so-called "masked developers," i.e. developer derivatives which do not act independently as developers but liberate the actual developers, for example after a cleavage or a dissociation reaction initiated by heat or by alkali. Masked developers of this kind and their use in photographic layers are described, for example, in German Pat. No. 1,246,406, in German Auslegeschrift 1,019,560, in British Pat. Nos. 632,836; 691,815; 783,887; 1,069,061 and 1,114,227 and in U.S. Pat. Nos. 3,243,294 and 3,342,599.

The nonphotosensitive image-receiving material usually consists of an arbitrary layer support, for example a transparent film or a suitable paper, for example a plastics-coated paper and a layer of binder which represents the image-receiving layer and which contains a dye mordant in order to fix the diffusing dyes.

Preferred mordants for acid dyes include long-chain quaternary ammonium or phosphonium compounds or ternary sulfonium compounds, for example of the kind described in U.S. Pat. Nos. 3,271,147 and 3,271,148, also certain metal salts and their hydroxides which form substantially insoluble compounds with the acid dyes.

The dye mordants are dispersed in the receiving layer in one of the usual hydrophilic binders, for example in gelatin, polyvinyl-pyrrolidone, completely or partially hydrolyzed cellulose esters. Some binders can, of course, also function as mordants, especially those of the kind which represents polymers of nitrogen-containing quaternary bases, for example polymers of N-methyl-2-vinyl pyridine of the kind described, for example, in U.S. Pat. No. 2,484,430, or polymers of aminoquinidine derivatives of alkyl vinyl ketones of the kind described, for example, in U.S. Pat. No. 2,882,156. However, other binders, for example gelatines, will usually be added to the last of these mordant binders.

In order to obtain multicolored images by the process according to the invention, the photosensitive material is initially immersed briefly in a developer solution following exposure behind a colored original, and then brought into effective contact with the nonphotosensitive receiving material which has also been impregnated with a developer solution. Silver halide is reduced at the exposed areas. The developer oxidation product formed splits the dye-giving compounds according to the invention and the dyes which have thus been rendered diffusible diffuse imagewise into the receiving layer where they are anchored by the mordant.

In the present context, effective contact means that the dye split off is able to diffuse between the photosensitive material and the image-receiving material. This does not necessarily mean that the layers of the photosensitive material containing the dye-giving compounds according to the invention and the image-receiving layer cannot be separated from one another by further colloid layers providing this does not prevent the dyes split off from diffusing.

In another embodiment of the process, the two elements may be arranged one above the other on the same layer support. In this case, the layer support initially carries the image-receiving layer containing a dye mordant and a binder, and above the image-receiving layer the various layers of the photosensitive material. The photosensitive layers are washed off following exposure and development and after the dyes which have been liberated imagewise by development have diffused into the lowermost image-receiving layer. In this case, readily soluble emulsions, for example of the kind based on polyvinyl alcohol or alkali-soluble cellulose ether phthalate, are generally used.

The liquid or pasty mixtures required to initiate the development process can, of course, also be accommodated in breakable containers or in rupturable pods that are split open under moderate mechanical pressure, and can be arranged, for example, between the photosensitive material and the nonphotosensitive image-receiving layer as described, for example, in U.S. Pat. Nos. 2,698,244; 2,559,643; 2,647,049; 2,661,293; 2,698,798 and 2,774,668. A composite material of this kind is eminently suitable for use in self-processing cameras. In this case, the containers accommodating the developing and activator solutions are arranged and dimensioned so that, following exposure, the contents are liberated as required in a quantity suitable for the development and the formation of diffusing dyes.

Suitable developers to be used in the process according to the invention include the color-forming developers commonly used in color photography, for example the usual aromatic, at least one primary amino group containing compounds of the

p-phenylene-diamine type. Suitable color-forming developers are for example N,N-dimethyl-p-phenylenediamine, N,N-diethyl-p-phenylenediamine, monomethyl-p-phenylenediamine 2-amino-5-diethyl-aminotoluene, N-butyl-N- ω -sulfoethyl-p-phenylenediamine, 2-amino-5-(N-ethyl-N- β -methanesulfonamidoethylamino)-toluene, N-ethyl-N- β -hydroxyethyl-p-phenylene-diamine, N,N-bis-(β -hydroxyethyl)-p-phenylenediamine or 2-amino-5-(N-ethyl-N- β -hydroxyethylamino)-toluene. Other suitable color-forming developers are described, for example, in J. Am. Chem. Soc. 73, 3,000 (1951).

However, one particular advantage of the process according to the invention is that the range of developer substances is not confined solely to the usual color-forming developers, instead black-and-white developers such as, for example, 4-aminophenol, 4-methyl aminophenol, 2-methylaminophenol or 3-methyl-4-aminophenol, can also be used for development. According to a preferred embodiment of the invention catechol and derivatives thereof can be used as developing substances, for example, catechol, 4-cyclohexylcatechol, 3-methoxycatechol, 4-(N-octadecylamino)-catechol or 5-dodecylamino-benzodioxolone-(2).

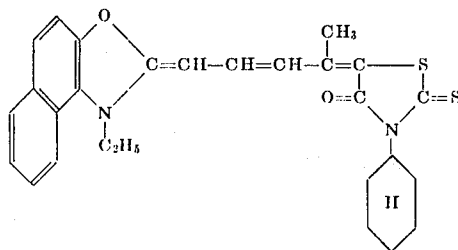
The baths normally used in conventional development processes, for example in color photography, can be used as developing baths in the process according to the invention. It is also possible however, to establish the prerequisites for optimum diffusion by varying the mineral salt content of the baths, the pH value, the viscosity and by adding organic solvents. As a rule, any competent expert need only conduct a few routine preliminary tests for this purpose.

EXAMPLE 1

A color photographic multiple-layer material is prepared as described in the following passage.

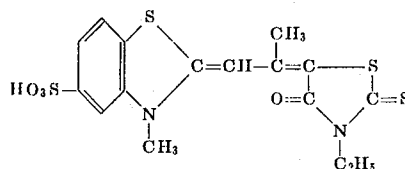
The layers mentioned in the following are cast in the order in which they are identified on to a layer support of pigmented cellulose triacetate.

1. A red-sensitive layer which, for 500 g. of an iodide-containing silver bromide emulsion (50 g. of silver per kg. of emulsion of which 4 mol percent are in the iodide form), contains 12 mg. of a red-sensitizer of the formula:



which sensitizer has been mentioned in example 11 of the German Auslegeschrift 1,213,240, 0.4 g. of saponin, 0.25 g. of N, N', N''-tris-acryloyl hexahydro-1,3,5-triazine as hardener and 5 g. of compound 2. Silver coating approximately 0.9 g./m.²

2. An intermediate layer of a 2 percent gelatin solution.
3. A green-sensitive layer which, for 500 g. of the iodide-containing silver bromide emulsion described in 1, contains 15 mg. of a green-sensitizer of the formula



which sensitizer has been described as dye No. 9 in German Auslegeschrift 1,177,481, 0.53 g. of saponin as wetting agent, 0.25 g. of N, N', N''-tris-acryloyl hexahydro-1,3,5-triazine and 6 g. of compound 11. Silver coating approximately 1 g./m.²

4. An intermediate layer of a 2 percent gelatin solution.
5. An unsensitized blue-sensitive emulsion layer which, for 500 g. of the iodide-containing silver bromide emulsion, described in 1, contains 0.3 g. of saponin, 0.25 g. of N, N', N''-tris-acryloyl hexahydro-1,3,5-triazine and 6 g. of compound 32. Silver coating approximately 0.9 g./m.²
6. A protective layer of a 2.5 percent gelatin solution.

The photographic material is exposed behind colored originals and then processed as follows:

The material is immersed for 45 seconds in a developer of the following composition:

- 5 g. of N,N-diethyl-p-phenylene diamine,
- 0.5 g. of potassium bromide,
- 1 g. of anhydrous sulfite,
- 25 g. of potassium carbonate,

made up with water to 1 liter, and the pH value adjusted to 11 with sodium hydroxide.

The photographic material is then brought into contact with an image-receiving layer which has also been immersed in the developer for 45 seconds. The image-receiving layer consists of a pigmented cellulose triacetate support, onto which the following layer is cast in a thickness of from 5 to 8 μ : a gelatin layer containing 20 g. of polyvinyl pyridine per kg. of 10 percent aqueous gelatin solution.

After the two materials have been left in contact for 6 minutes, they are separated and the image-receiving material rinsed thoroughly with water for 3 minutes and then dried. A full color negative of the original with a maximum density of around 2 is obtained.

EXAMPLE 2

Similar good results are obtained, if the material as described in example 1 is treated with one of the following developers:

- A.
 - 3 g. of catechol
 - 0.3 g. of potassium bromide
 - 25 g. of potassium carbonate
 - 0.5 g. of anhydrous sodium sulfite
 - 1 g. of ascorbic acid
 - water up to 1,000 ml.
 - pH adjusted to 12.
- B. In the developer A catechol is replaced by 3 g. of 4-cyclohexylcatechol.
- C.
 - 3 g. of catechol
 - 0.05 g. of 1-phenyl-3-pyrazolidone
 - 0.3 g. of potassium bromide
 - 25 g. of potassium carbonate
 - 0.5 g. of anhydrous sodium sulfite
 - 1 g. of ascorbic acid
 - water up to 1,000 ml.
 - pH adjusted to 12.
- D.
 - 10 g. of 2-amino-5-(N-butyl-N-hydroxyethylamino)-toluene (salt of naphthalene-1,5-disulfonic acid)
 - 0.5 g. of potassium bromide
 - 1 g. of anhydrous sodium sulfite
 - 25 g. of potassium carbonate
 - water up to 1,000 ml.
 - pH adjusted to 11.
- E. In the developer D the developing agent mentioned is replaced by 5 g. of 2-amino-5-(N-ethyl-N-hydroxyethylamino)-toluene $\cdot$ H₂SO₄.
- F. In the developer D the developing agent mentioned is replaced by 15 g. of 2-amino-5-(N-ethyl-N- β -methanesulfonamidoethylamino)-toluene-sulfate.
- G. In the developer A catechol is replaced by 5 g. of 3-methoxycatechol.

EXAMPLE 3

A color photographic multilayer material is prepared as described in the following.

- 5 The following layers are successively cast on to a layer support of white-pigmented cellulose triacetate:
 1. A gelatin layer which, per kg. of 5 percent aqueous gelatin solution contains 30 g. of trimethyl octadecyl ammonium sulfate, 0.4 g. of saponin and 0.3 g. of N,N',N''-tris-acryloyl hexahydro-1,3,5-triazine as hardener. This layer is cast in a thickness of 8 μ .
 2. A sodium alginate layer approximately 1.0 μ thick.
 3. A green-sensitized layer similar to layer 3 of example 1 which contains 0.3 g. of saponin, 0.25 g. of N,N',N''-tris-acryloyl hexahydro-1,3,5-triazine as hardener and 6 g. of the compound 34. Silver coating 0.9 g./m.²
 4. An intermediate layer of a 2 percent aqueous gelatin solution.
 5. A red-sensitized layer similar to layer 1 of example 1 which contains 0.4 g. of saponin, 0.25 g. of N,N',N''-tris-acryloyl hexahydro-1,3,5-triazine and 6 g. of the compound 2. Silver coating 0.8 g./m.²
 6. An intermediate layer of a 2 percent aqueous gelatin solution.
 7. An unsensitized blue-sensitive emulsion layer which, for 500 g. of the iodide-containing silver bromide emulsion described in 1 of example 1, contains 0.2 g. of saponin, 0.25 g. of N,N',N''-tris-acryloyl hexahydro-1,3,5-triazine as hardener and 7 g. of compound 12. Silver coating approximately 0.8 g./m.²
 8. A protective layer of a 2.5 aqueous gelatin solution to which the usual hardeners and wetting agents have been added.

35 The color photographic material is exposed behind a multicolored original and processed as follows:

The material is immersed for 30 seconds in a developer of the following composition:

- 40
 - 10 g. of N-ethyl-N- ω -hydroxyethyl-p-phenylene diamine,
 - 0.8 g. of potassium bromide,
 - 20 g. of potassium carbonate,
 - 0.5 g. of anhydrous sodium sulfite, and
 - 1 g. of hydroxyethyl cellulose

made up with water to 1 liter. The pH is adjusted to 11 with sodium hydroxide.

45 The material is then removed from the developer. After a contact time of 2 minutes, the developer and the emulsion layers are removed with concentrated jet of water. A full-colored negative of the original with brilliant colors and deep blacks is obtained after drying.

EXAMPLE 4

50 A green-sensitized silver bromoiodide emulsion which contains per kg. 48 g. of silver and thereof 4 mol percent in the iodide form and to which have been added per kg. 15 g. of dye-giving compound 17, and 8 g. of 4-(N-octadecoylamino)-catechol is coated on to a layer support of cellulose triacetate. Silver coating 1.3 g. per m.²

60 This material is exposed behind a green step wedge and is immersed for 30 seconds in an activator bath of the following composition:

- 65
 - 1.5 g. ascorbic acid
 - 0.5 g. of potassium bromide
 - 0.03 g. of 1-phenyl-3-pyrazolidone
 - 20 g. of potassium carbonate
 - water up to 1,000 ml.
 - pH adjusted to 11.

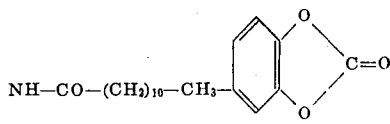
70 The material is then brought into contact with an image-receiving material which consists of a layer support of cellulose triacetate on to which has been coated a 10 percent aqueous gelatin solution containing per kg. 35 kg. of trimethyl octadecyl ammonium sulfate; layer thickness 4 μ .

75 After the two materials have been left in contact for 3 minutes they are separated. A negative wedge is obtained in

the image-receiving layer having a maximum density of 1.55 and a minimum density of 0.13.

EXAMPLE 5

In the material of example 4 the derivative of catechol used is replaced by 12 g. of the compound of the formula:



A solution of the following composition is used as activator:

0.8 g. of anhydrous sodium sulfite
0.5 g. of potassium bromide
0.03 g. of 1-phenyl-3-pyrazolidone
25 g. of potassium carbonate
water up to 1,000 ml.
pH adjusted to 12.

After processing a magenta wedge is obtained having a maximum density of 1.2 and a minimum density of 0.2.

EXAMPLE 6

A 10 percent aqueous gelation solution which contains per kg. 20 g. of dye-giving compound 34 and 15 mg. of silver sulfide is coated onto a layer support of cellulose triacetate; layer thickness 1.8μ. As a second layer is coated thereon a green-sensitive silver bromiodide emulsion, which contains per kg. 64 g. of silver and 4 mol percent thereof in the form of iodide; silver coating 1.6 g. per m.²

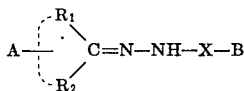
After exposing behind a green step wedge, the material is dipped for 30 seconds into a developing mixture of the following composition:

10 g. of N-ethyl-N-hydroxyethyl-p-phenylene-diamine
0.5 g. of anhydrous sodium sulfite
0.5 g. of sodium thiosulfate
0.5 g. of potassium bromide
20 g. of potassium carbonate
water up to 1,000 ml.
pH adjusted to 11.6.

Then the material is brought into contact for 3 minutes with a image-receiving material as described in example 4. After separation of the two materials a positive magenta wedge is obtained in the image-receiving material having a maximum density of 1.38 and a minimum density of 0.23.

We claim:

1. A color photographic diffusion transfer process for the production of color images, which comprises forming a pattern of developable silver halide in a light-sensitive photographic material comprising at least one silver halide emulsion layer and having distributed therein or in an adjacent layer a dye-giving compound being resistant to diffusion during development in the presence of an alkaline developing solution, capable of forming a diffusible acid dye on reaction with developer oxidation products and having the formula:



in which

R₁ represents hydrogen, alkyl with up to 20 carbon atoms, aryl or amino substituted by alkyl or aryl, in which case two alkyl groups on the nitrogen can be closed together to form a ring;

R₂ represents alkyl with up to 20 carbon atoms, aryl, acyl derived from an aliphatic carboxylic acid with up to 20

carbon atoms or an aromatic carboxylic acid, or amino substituted by alkyl or aryl, in which case two alkyl groups on the nitrogen can be closed together to form a ring; or

R₁ and R₂ together represent the ring members required to complete an isocyclic or heterocyclic group; 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;

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

B represents a dye radical; or

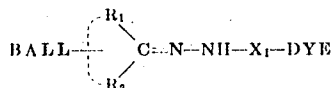
A represents a dye radical either on its own or in conjunction with R₂; and

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

treating said material with an alkaline developing solution in the presence of a developing agent and developing said pattern of developable silver halide, said dye-giving compound

20 reacting with the oxidation product of the developing agent during the development and thereby releasing a diffusible acid dye image in the area of development, during the course of said development said dye image being transferred by diffusion wholly or in part to an image-receiving layer containing a basic mordant for acid dyes.

2. A color photographic diffusion transfer process as claimed in claim 1, wherein as dye-giving compound a compound of the following general formula is used:



in which:

R₁ represents hydrogen, alkyl with up to 20 carbon atoms, aryl or amino substituted by alkyl or aryl, in which case two alkyl groups on the nitrogen can be closed together to form a ring;

R₂ represents alkyl with up to 20 carbon atoms, aryl, acyl derived from aliphatic carboxylic acids with up to 20 carbon atoms or aromatic carboxylic acids, or amino substituted by alkyl or aryl, in which case two alkyl groups on the nitrogen can be closed together to form a ring; or

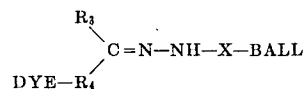
R₁ and R₂ together represent the ring members required to complete an isocyclic or heterocyclic ring; at least one of the radicals R₁ and R₂ carries the group BALL;

X represents a sulfonyl group or a carbonyl group;

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

DYE represents a dye radical.

3. A color photographic diffusion transfer process as claimed in claim 1, wherein as dye-giving compound a compound of the following general formula is used:



in which

R₃ represents hydrogen, alkyl or aryl.

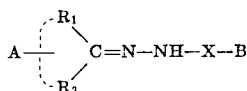
R₄ represents an aryl group which can be part of the chromophoric system of the dye radical;

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; and

DYE represents a dye radical either on its own or together with R₄.

4. A color photographic diffusion transfer process for the production of color images, which comprises exposing to a visible subject a light-sensitive photographic material comprising superposed red, green, and blue light-sensitive silver halide emulsion layers and having distributed therein or in layers adjacent thereto dye-giving compounds being resistant to diffusion during the development in the presence of an alkaline developing solution, capable of forming a cyan, magenta, and yellow diffusible acid dye on reaction with developer oxidation products and having the formula:



in which

R₁ represents hydrogen, alkyl with up to 20 carbon atoms, aryl or amino substituted by alkyl or aryl, in which case two alkyl groups on the nitrogen can be closed together to form a ring;

R₂ represents alkyl with up to 20 carbon atoms, aryl, acyl derived from an aliphatic carboxylic acid with up to 20 carbon atoms or an aromatic carboxylic acid, or amino substituted by alkyl or aryl, in which case two alkyl groups on the nitrogen can be closed together to form a ring; or

R₁ and R₂ together represent the ring members required to complete an isocyclic or heterocyclic group; 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 on its own or in conjunction with R₂; and

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

treating said material with an alkaline developing solution in the presence of a developing agent and developing said imagewise exposed material, said dye-giving compounds reacting with the oxidation product of the developing agent during the development and thereby releasing each a cyan, magenta and yellow diffusible acid dye image in the areas of development, during the course of said development said dye images being transferred by diffusion wholly or in part imagewise in register to an image-receiving layer containing a basic mordant for acid dyes.

5. A process as claimed in claim 4 wherein, after the beginning of development, the photosensitive material is brought into intimate contact with the image-receiving layer and is separated from it again after the dye images have been transferred to form a color image in said image-receiving layer.

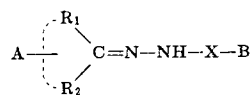
6. A process as claimed in claim 4, wherein, before the beginning of development, the photosensitive material is in intimate contact with the image-receiving layer and is separated from it after the dye images formed by development have been transferred to form a color image in said image-receiving layer.

7. A process as claimed in claim 4, wherein development is carried out by an alkaline liquid or viscous developer or activator solution in the presence of a developing agent containing a primary amino group.

8. A process as claimed in claim 4, wherein development is carried out by an alkaline liquid as viscous developer or activator solution in the presence of catechol or a derivative of catechol as developing agent.

9. A light-sensitive color photographic material comprising at least one silver halide emulsion layer and containing distributed therein or in a layer adjacent thereto a dye-giving compound being resistant to diffusion during development in the presence of an alkaline developing solution, capable of forming a diffusible dye on reaction with developer oxidation

products and having the formula:



in which

R₁ represents hydrogen, alkyl with up to 20 carbon atoms, aryl or amino substituted by alkyl or aryl, in which case two alkyl groups on the nitrogen can be closed together to form a ring;

R₂ represents alkyl with up to 20 carbon atoms, aryl, acyl derived from an aliphatic carboxylic acid with up to 20 carbon atoms or an aromatic carboxylic acid, or amino substituted by alkyl or aryl, in which case two alkyl groups on the nitrogen can be closed together to form a ring; or

R₁ and R₂ together represent the ring members required to complete an isocyclic or heterocyclic group; 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;

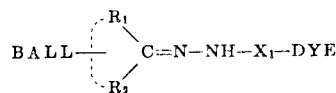
A represents a photographically inert radical rendering the dye-giving compound resistant to diffusion; and

B represents a dye radical; or

A represents a dye radical either on its own or in conjunction with R₂; and

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

10. A color photographic material is claimed in claim 9 which contains as dye-giving compound a compound of the following general formula:



in this formula:

R₁ represents hydrogen, alkyl with up to 20 carbon atoms, aryl or amino substituted by alkyl or aryl, in which case two alkyl groups on the nitrogen can be closed together to form a ring;

R₂ represents alkyl with up to 20 carbon atoms, aryl, acyl derived from aliphatic carboxylic acids with up to 20 carbon atoms or aromatic carboxylic acids, or amino substituted by alkyl or aryl, in which case two alkyl groups on the nitrogen can be closed together to form a ring; or

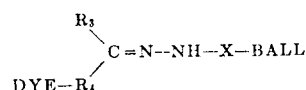
R₁ and R₂ together represent the ring members required to complete an isocyclic or heterocyclic group; at least one of the radicals R₁ and R₂ contains the group BALL;

X₁ represents a sulfonyl group or carbonyl group;

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

DYE represents a dye radical.

11. A color photographic material as claimed in claim 9, which contains as dye-giving compound a compound of the following general formula:



in this formula

R₃ represents hydrogen, alkyl or aryl;

R₄ represents an aryl group which can 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; and

DYE represents a dye radical either on its own or together with R₄.

* * * * *

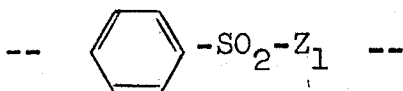
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,628,952 Dated December 21, 1971

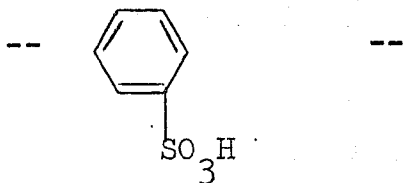
Inventor(s) Walter Puschel et al

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

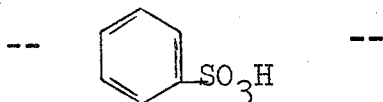
Column 7, compound 9, right hand part of formula should read as follows:



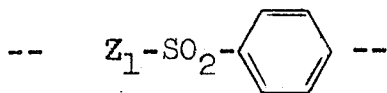
Column 8, compound 16, the middle part of the formula should read as follows:



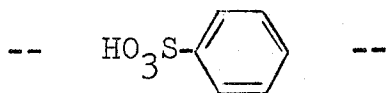
Column 9, compound 18, the right side of the formula should read as follows:



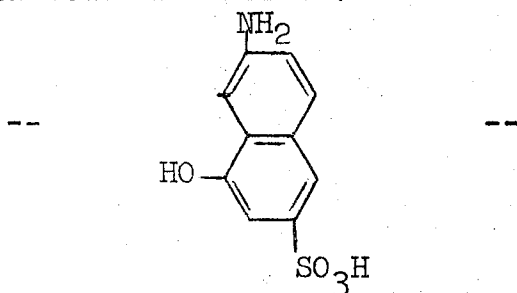
Column 9, compound 19, left side of the formula should read as follows:



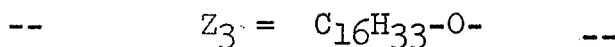
Column 10, compound 27, left side of the formula should read as follows:



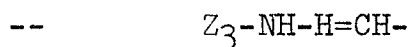
Column 12, compound 36, the right side of the formula should read as follows:



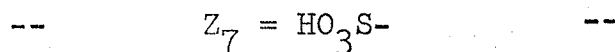
Column 12, compound 37, the right side of the formula should read as follows:



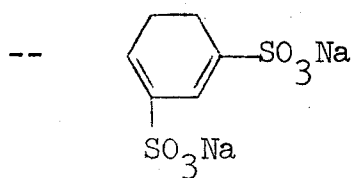
Column 13, compound 48, the left side of the formula should read as follows:



Column 18, bottom formula, the left side should read as follows:



Column 21, compound 103, right side of formula should read as follows:

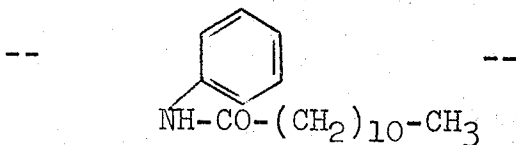


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Inventors Walter Puschel et al

Dated December 21, 1971

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Column 29, in Example 5, the right side of the formula should read as follows:



Column 6, lines 43 - 61, the text therein is a reiteration of the top of column 6 and should be deleted.

Signed and sealed this 10th day of April 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents