United States Patent [19]

Morcher et al.

[11] **3,859,095**

[45] **Jan. 7, 1975**

[54] **COLOR-PHOTOGRAPHIC MATERIAL WITH IMPROVED COLOR REPRODUCTION**

[75] Inventors: **Bernhard Morcher,** Leverkusen; **Helmut Mader,** Odenthal-Hahnenberg, both of Germany

[73] Assignee: **Agfa-Gevaert Aktiengesellschaft,** Leverkusen, Germany

[22] Filed: **Feb. 26, 1973**

[21] Appl. No.: **335,577**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 95,851, Dec. 7, 1970, abandoned.

[30] **Foreign Application Priority Data**

Dec. 13, 1969 Germany 1962606

[52] **U.S. Cl.** **96/74,** 96/9, 96/22, 96/100

[51] **Int. Cl.** **G03c 1/76**

[58] **Field of Search** 96/100, 74, 9

[56] **References Cited**

UNITED STATES PATENTS

2,298,443	10/1942	Weissberger	96/100
2,474,293	6/1949	Weissberger et al.	96/100
2,808,329	10/1957	Whitmore	96/100
2,852,370	9/1958	Whitmore	96/100
2,860,975	11/1958	Whitmore et al.	96/100

Primary Examiner—J. Travis Brown

Attorney, Agent, or Firm—Connolly and Hutz

[57] **ABSTRACT**

In a color photographic multiplelayer material having diffusion-fast dyes and containing colorless color-forming couplers and colored masking couplers in at least one layer and which remain in the layer and contribute to the production of the same partial color image, the couplers differing in their coupling reactivity wherein good masking is achieved, by providing the more reactive colorless coupler in contrast to the less reactive colored coupler, dispersed in the particular layer in the form of small particles or droplet of a water-insoluble organic crystalloid solvent with a boiling point above 175°C. The couplers contain an alkyl radical attached to the coupler molecule in an non-coupling position.

2 Claims, 13 Drawing Figures

FIG. 1

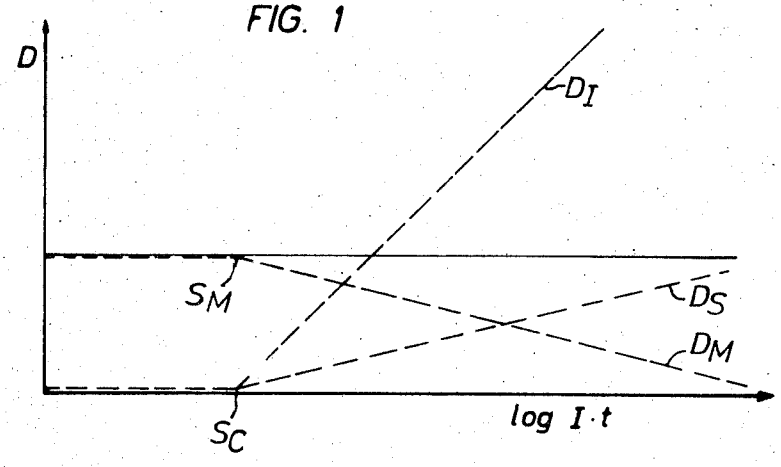


FIG. 2

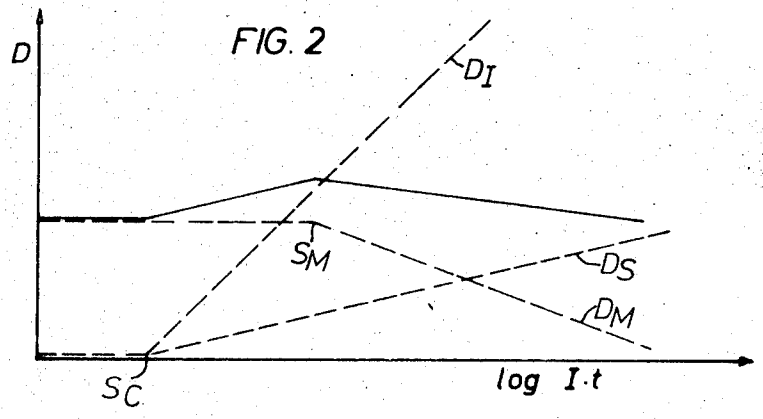
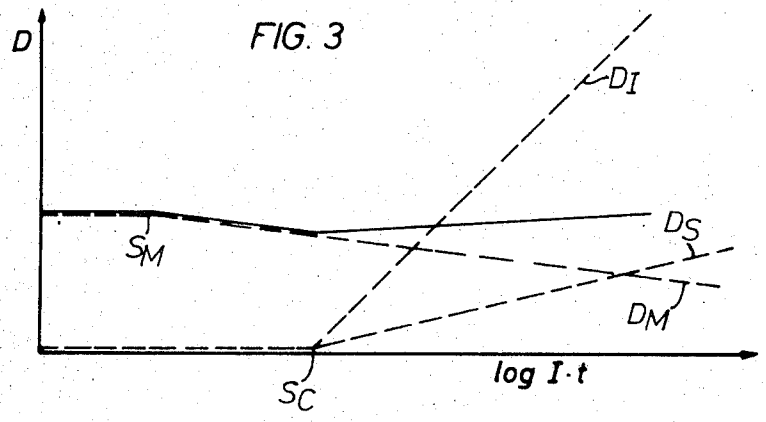


FIG. 3



INVENTOR:

BERNHARD MORCHER, HELMUT MÄDER.

FIG. 4

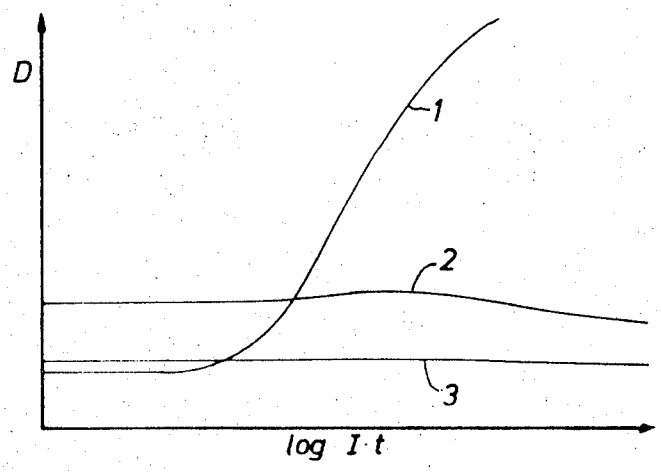


FIG. 5

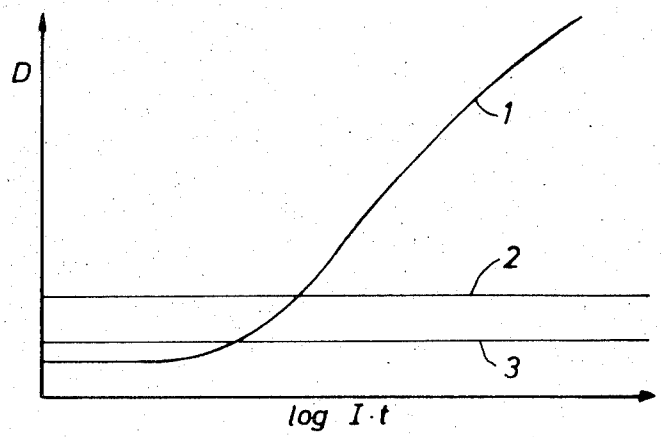


FIG. 6

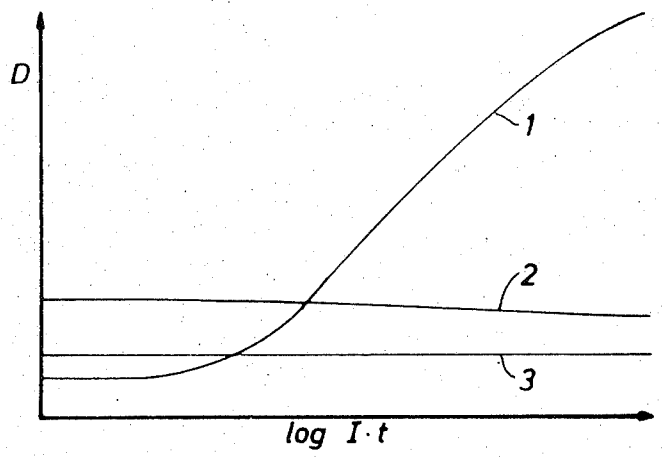


FIG. 7

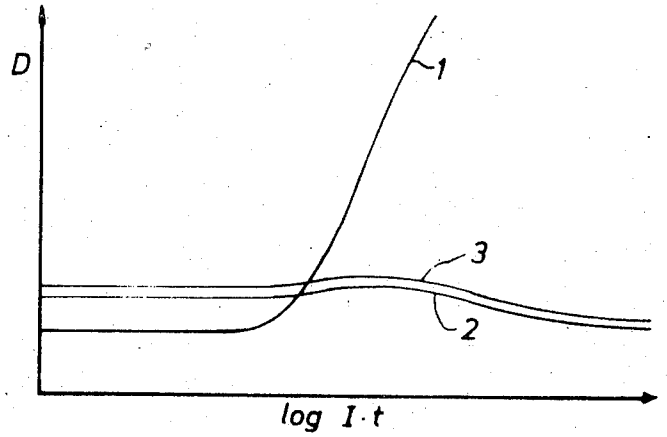


FIG. 8

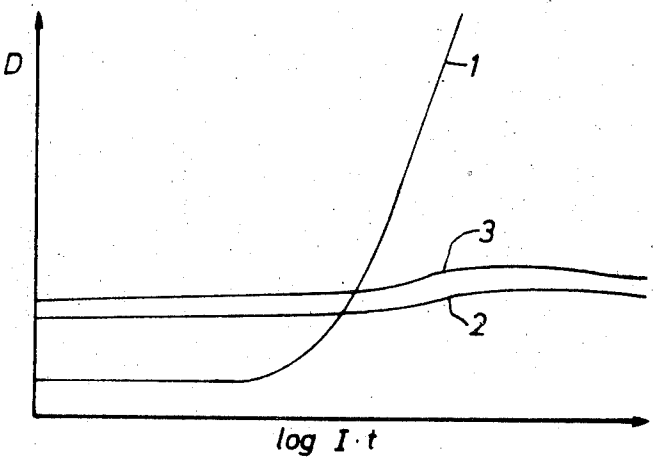
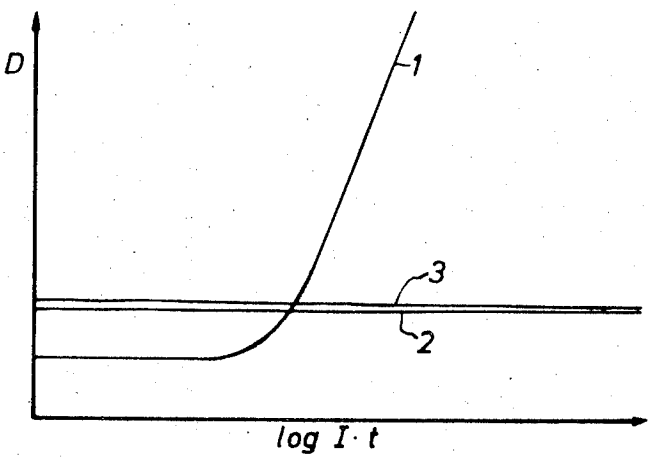


FIG. 9



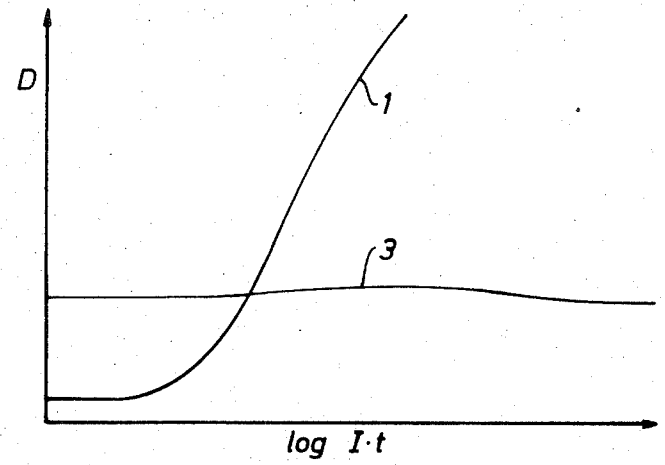


FIG. 10

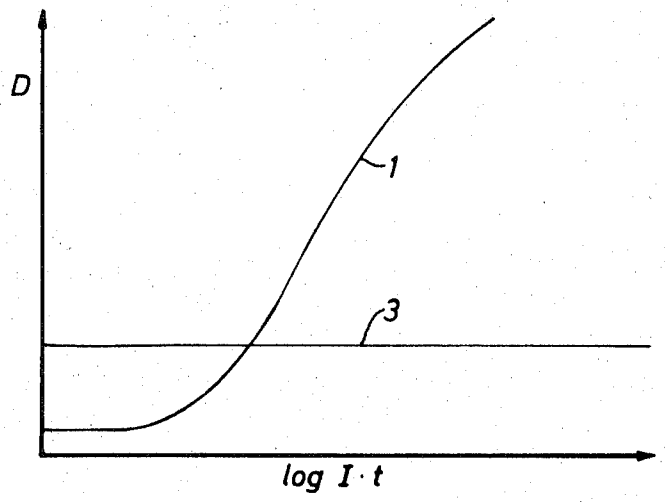


FIG. 11

FIG. 12

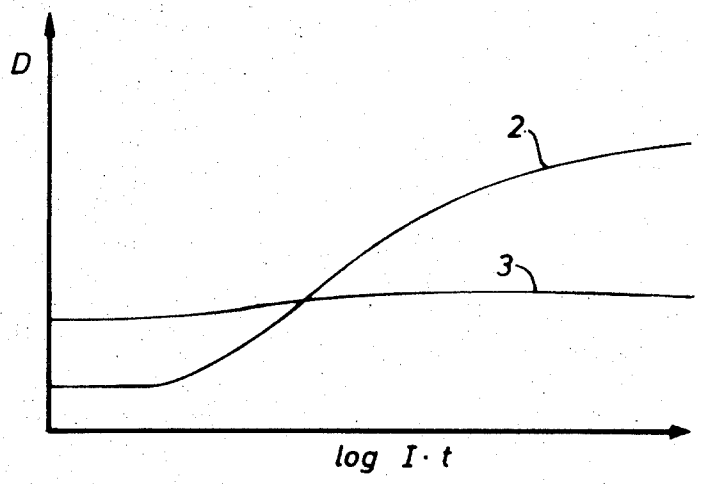
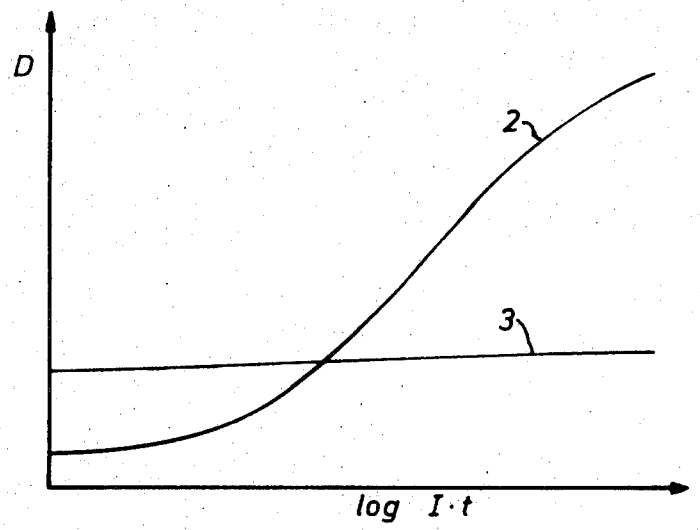


FIG. 13



COLOR-PHOTOGRAPHIC MATERIAL WITH IMPROVED COLOR REPRODUCTION

This application is a continuation-in-part of the copending, now abandoned U.S. Pat. application Ser. No. 95,851, filed Dec. 7, 1970 for Color-Photographic Material with Improved Color Reproduction.

This invention relates to a color photographic material with improved color reproduction, containing colored couplers for producing so-called built-in masks.

It is known that the undesirable side densities of the image dyes formed during the chromogenic development of color photographic multiple-layer materials can be compensated by masking processes. In the case of color photographic materials, this can be done by using so-called built-in masks. Masks of this kind can be produced, for example, during the photographic processing by using masking couplers which themselves have a color corresponding to the undesirable side density of the image dyes to be masked. Color-forming couplers suitable for this purpose usually have the same chemical stucture as conventional color-forming couplers except that in the coupling position they contain a group which provides the color-forming coupler with its colour, usually an aryl azo group, and which is eliminated during the reaction with the oxidized color-forming developer. Accordingly, color-forming development of an exposed photographic material containing a masking coupler is accompanied by formation of the required image dye from the colored masking coupler and hence the undesirable side density of the image dye as well, depending upon the quantity of silver halide which has been rendered developable by exposure. At the same time, however, the color density of the masking coupler is also weakened. The masking effect is obtained by virtue of the fact that the unconsumed masking coupler has a gradation opposite so that of the undesirable side density of the image dye.

In general, however, it has been found that the extinction coefficient of conventional masking couplers, as measured at the wavelength of maximum absorption, is considerably higher than that of the side color density of the corresponding image dyes formed from the couplers. The overmasking effect attributable to this can be eliminated in known manner by combining the masking coupler with a certain quantity of a second colorless coupler which during chromogenic development gives the same image dye or a similar image dye. In an optimally masked material, the gradation of the undesirable side density of the image dye obtained during processing is superimposed by the equally high but oppositely directed gradation of the masking dye so that a uniform density unaffected by exposure is obtained in the spectral region of the undesirable side density. In the case of an effectively masked cyan-forming coupler, for example, after the processing the yellow side density measured behind a blue filter and the magenta side density measured behind a green filter are constant and unaffected by exposure. In practice, this objective is achieved by determining a suitable quantitative ratio between the colored masking coupler and the colorless added component. The side densities of the image dyes (yellow in the case of magenta-forming couplers and magenta and yellow in the case of cyan-forming couplers) are intended to be completely free from any gradation.

Another requirement which has to be satisfied in order to obtain effective masking of the undesirable side density of the image dyes is that there should be adequate consistency between the colorless coupler and the masking coupler in regard to their kinetic properties. Both couplers should also have the same photographic sensitivity under comparable conditions since they are, of course, to be used in the same emulsion.

The importance of this requirement is discussed in the following with reference to

FIGS. 1 to 3 which show the characteristic curves of coupler/masking coupler combinations.

In the Figures, the density (D) is plotted against the exposure (Log. I.t). The main density (image density) and side density of the image dye are presented by broken lines D_I and D_S, whilst the broken line D_M represents the masking density. The continuous line is obtained by adding the side density of the image dye to the masking density and thus represents the over all density in the spectral region of the side density of the image dye to be masked. In the case of an ideally masked material, this line is a straight line which is unaffected by exposure. S_C and S_M represent the relative sensitivities of the coupler and the masking coupler.

Accordingly, it is quite clear from FIGS. 1 to 3 that optimum masking can only be obtained where the relative sensitivities of the coupler and masking coupler are consistent with one another (FIG. 1; $S_C = S_M$). In every other case (FIGS. 2 and 3) the masking effect obtained is totally inadequate.

However, it has been found that in the majority of cases the sensitivity of the colorless couplers is higher than that of the corresponding masking coupler. This may be attributable to the fact that during color coupling of the masking coupler the arylazo group has to be eliminated from the coupler molecule which clearly retards dye formation. Accordingly, most coupler/-masking coupler combinations give only an inadequate masking effect.

Some proposals have already been put forward with a view to overcoming this deficiency. For example, it has been proposed to replace the colorless 4-equivalent couplers by corresponding similarly colorless 2-equivalent couplers. In the coupling position, couplers of this kind carry a substituent, for examle a halogen such as chlorine or bromine, a sulfo group or a carboxyl group or a radical attached through a thioether bridge which has to be eliminated during coupling and hence retards dye formation. It is possible in this way to adapt the colorless couplers in their reactivity towards the colored masking couplers which, of course, are also 2-equivalent couplers. However, it has been found that 2-equivalent couplers show a pronounced tendency toward fogging. Although some fogging was inevitable in the case of masked materials due to the use of the colored couplers, a further increase in color fogging attributable to colorless 2-equivalent couplers is not acceptable on account of the additional falsification of color which this produces.

According to U.S. Pat. No. 2,688,539, it is proposed to use colorless couplers and masking couplers in separate emulsion layers, in which case the lower reactivity of one of the couplers can if necessary be compensated by increasing the sensitivity of the corresponding silver halide emulsion. Unfortunately, the production of a material of this kind involves considerable technical outlay on account of the additional layers required.

In U.S. Pat. No. 2,808,329 to Whitmore combinations of a colored masking coupler and a colorless colorforming coupler are described wherein the colorless coupler is incorporated by means of a coupler solvent. However the colored masking couplers of this reference are of the type forming on colorforming development a soluble dye that easily is washed out of the layer and thus does not contribute to the final partial color image.

Accordingly, the object of the invention is to provide a color photographic material containing a colored coupler which can be used in the usual way for producing color photographs with improved color reproduction and which does not have any of the disadvantages referred to above.

It is a further object of this invention to provide light-sensitive color photographic material which contains a colorless coupler and a colored coupler having different coupling speeds and both forming on colored development dyes of substantially the same color that remain in the layer and contribute to the same partial image which are adapted with regard to reactivity by incorporating the fast coupler in an oil former whereas the slower coupler is incorporated without an oil former and which are also adapted with regard to diffusion-fastness by containing a radical attached to the coupler molecule in a non-coupling position to provide non-diffusibility.

According to the invention a color photographic material containing color-forming couplers is provided, which in at least one light sensitive silver halide emulsion layer or in a hydrophilic colloid layer immediately adjacent thereto contains a combination of a colorless coupler and a colored masking coupler for the production of the partial image, the couplers differing in their coupling reactivity and the more reactive coupler, in contrast to the less reactive coupler, being dispersed in the silver halide emulsion layer or in an adjacent layer in the form of small particles or droplets of a solution in a water-insoluble organic crystalloid solvent with a boiling point above 175°C. In general, color photographic materials are multiple-layer materials containing at least three photosensitive silver halide emulsion layers with different spectral sensitivity for producing a yellow, a magenta and a cyan partial color image. The order in which the layers occur can be changed as required although in practice it is governed by certain criteria outside the scope of the invention. A widely used material, for example, carries a red-sensitive layer containing a cyan-forming coupler on the (usually transparent) layer support, above this layer a green-sensitive layer containing a magenta-forming coupler and, as the uppermost layer, a blue-sensitive layer containing a yellow-forming coupler. Other sequences may also occur. Naturally, the color-forming coupler does not necessarily have to be present in the same layer with the correspondingly sensitized silver halide. It is also possible to accommodate it in a colloid layer immediately adjacent the silver halide emulsion layer. In color photography, masking problems are as a rule only encountered during production of the magenta and the cyan partial images. The yellow partial image normally does not have any troublesome side density. Accordingly, in practice it is only colorless magneta-forming and cyan-forming couplers that are combined with a corresponding colored coupler for masking purposes, whilst in general

for the production of the yellow partial image only colorless couplers are used.

Numerous coupler/masking coupler pairs which in so far as their spectral properties are concerned would be eminently suitable for producing the masked magenta or cyan partial image, i.e., in which case identical or substantially identical dyes are formed from the coupler and the masking coupler whilst the color of the masking coupler corresponds to the side density of the image dye to be masked, cannot be used for masking purposes simply because the coupler and the masking coupler do not react at the same velocity with the oxidation product of the color-forming developer. According to the invention, this deficieny is eliminated by introducing the more reactive coupler in solution in an organic crystalloid solvent, a so-called oil-former, into the emulsion whilst the less reactive coupler is incorporated into the emulsion without using such as oilformer.

In the present context, the expression coupling reactivity or sensitivity refers to the relative coupling velocity of the couplers during their reaction with the oxidation product of the color-forming developer. The relative coupling velocity can be measured by conventional methods. One particularly suitable method is described for example by J. Eggers in "Mitteilungen aus den Forschungslaboratorien der Agfa Leverkusen-Muenchen", Vol.III, page 81 (Springer-Verlag Berlin, Goettingen, Heidelberg 1961). However, it is not absolutely necessary quantitatively to determine the coupling velocity, rather is it sufficient to decide purely phenomenologically which of the couplers is the more reactive under comparable conditions. In the case of coupler/-masking coupler pairs, this can be deduced for example from the shape of the side density gradation curve. Gradation curves of this kind are shown in FIGS. **1** to **3** (continuous line). In FIG. **1**, both couplers have the same reactivity whilst in FIG. **2** the colorless coupler is more reactive and in FIG. **3** it is less reactive than the colored coupler.

Occasionally, the colored coupler of a suitable coupler/masking coupler pair may have the higher level of reactivity. However, this case is more the exception than the rule, and in general, the colorless coupler is the more sensitive.

Accordingly, in one particularly advantageous embodiment of the invention, the color photographic material contains at least three photosensitive silver halide emulsion layers, namely a red-sensitive, a green-sensitive and a blue-sensitive silver halide emulsion layer, at least one of the first two silver halide emulsion layers being associated with a combination of a more reactive colorless coupler and a less reactive colored masking coupler for producing the partial color image complementary to the particular range of the spectrum, to which the layer is sensitive, whilst the more reactive colorless coupler is dispersed in the particular layer in the form of small particles of a solution in a water-insoluble organic crystalloid solvent with a boiling point above 175°C.

The present invention is based upon the principle that different coupling speeds of a colorless coupler and a colored coupler can be adapted with regard to reactivity by incorporating the faster coupler in an oil former. To this is added the fact that the couplers contain a radical attached to the coupler molecule in a non-coupling position which provides non-diffusibility.

This is a long-chain alkyl radical having at least 6 carbon atoms.

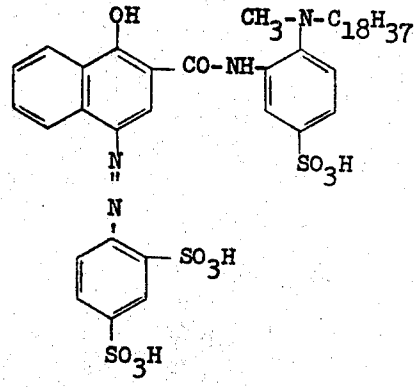
The diffusion-preventing radical attached to the coupler molecule in the non-coupling position prevents diffusion of the couplers, colorless and colored couplers, into other layers, which diffusion is undesirable. The diffusion-resistant radicals are sufficiently resistant to washing out of the photographic material so that they remain in the photographic material after the usual method of color-forming development of an exposed material containing the couplers and the formation of the required image dye.

The following, inter alia, are suitable diffusion-resisting groups:

$-C_{18}H_{37}$, $-C_{16}H_{33}$

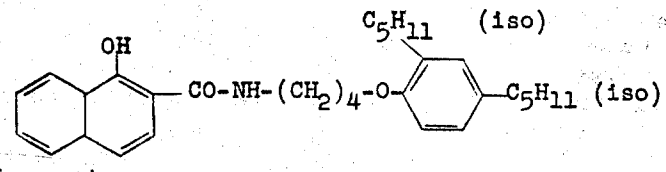
Compounds of the following general formulae are examples of suitable colored and colorless couplers:

Masking coupler:



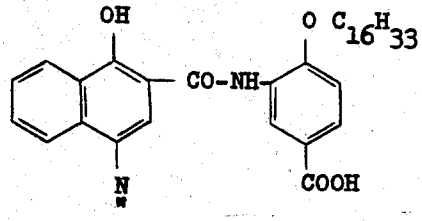
(1)

Colorless coupler:

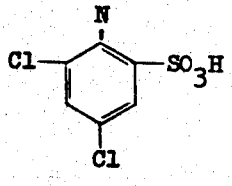


(1')

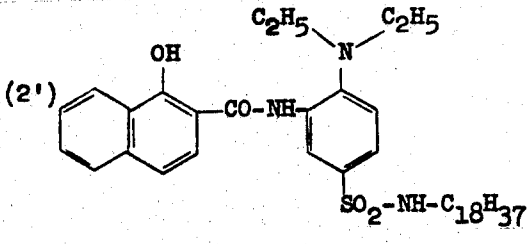
Masking coupler:



(2)

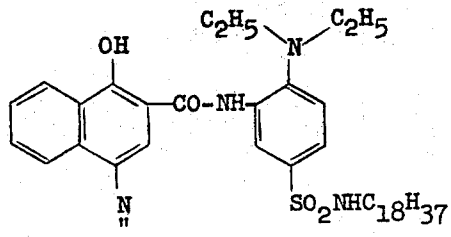


Colorless coupler:

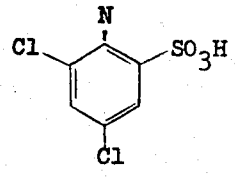


(2')

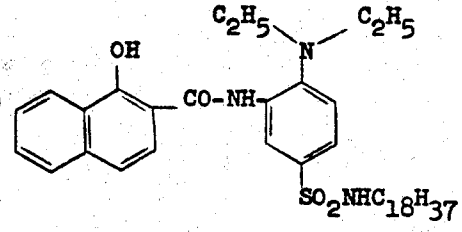
Masking coupler:



(4)

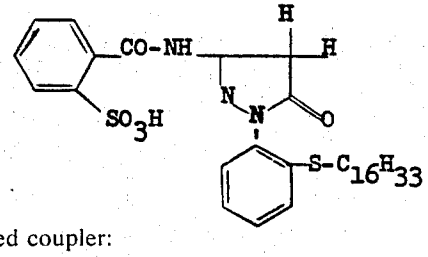


Colorless coupler:



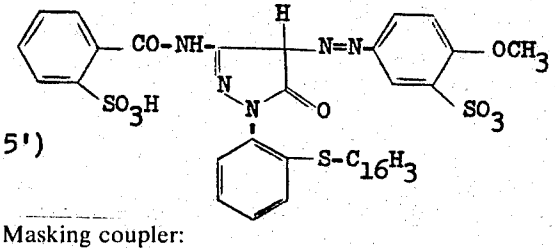
(4')

Colorless coupler:



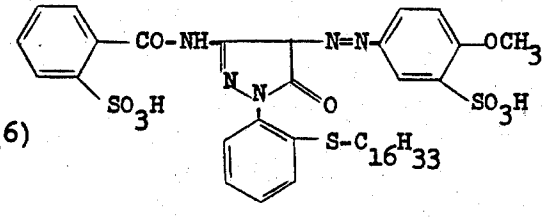
(5)

Colored coupler:



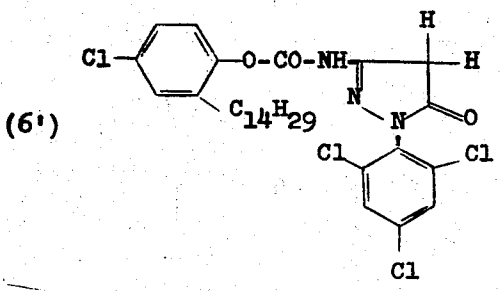
(5')

Masking coupler:



(6)

Colorless coupler:



(6')

The color photographic material according to the invention is prepared in the usual way by successively applying the different photosensitive layers and, optionally, non-photosensitive intermediate layers, on to a generally transparent layer support or substrate. The less reactive coupler, usually the colored masking coupler, is added to the silver halide emulsion, or another layer-forming colloid by one of the known methods, for example in the form of an aqueous-alkaline solution, or by dispersing a solution in a low boiling organic solvent. Examples of suitable low boiling organic solvents include nitromethane, nitroethane, lower alkyl esters of formic acid or acetic acid such as ethyl acetate, butyl acetate and ethyl formate.

The more reactive coupler, which is usually the colorless coupler, is dissolved together with the so-called oilformer in a low boiling organic solvent of the aforementioned kind and dispersed in this form either in the emulsion or in another layer-forming colloid. Following evaporation of the low boiling solvent, the coupler is then present in a heterogeneous phase in the form of oily droplets or of particles of a solution in the oilformer. In some cases, it is also possible to omit the low boiling solvent altogether and to dissolve the coupler in the oilformer, optionally at an elevated temperature.

In the context of the invention, oilformers are the conventional water-insoluble coupler solvents which are occasionally referred to in the literature as crystalloid solvents which are described, for example, in U.S. Pat. Nos. 2,304,940 and 2,322,027. The solvents in question are high boiling, organic, low molecular weight compounds which are able to penetrate through semipermeable membranes and which generally boil at temperatures above 175°C. At room temperature, i.e., at 20°C, they are usually liquid or melt at relatively low temperatures, i.e., at temperatures below 100°C. They are known as oilformers because they usually form oily or liquid solutions in admixture with couplers.

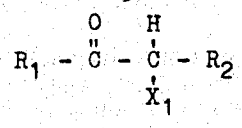
Examples of particularly advantageous coupler solvents include compounds of the kind containing one or more polar groups or atoms, for example hydroxyl-, carboxylic-, amide and keto groups and halogen atoms. Their dissolving effect upon the coupler should be as high as possible and the solvents should of course be inert to the silver halide emulsions into which they are incorporated. Naturally, they should also be colorless where possible, they should remain stable under the effect of light, heat and moisture and in addition should be inert to the different developing and treatment baths in which the color photographic material is developed. Furthermore, they should be substantially involatile. In some cases, it has proved to be of advantage to use a mixture of two or more different crystalloid compounds or coupler solvents to prepare the coupler dispersion. This is especially advantageous where the compounds in question have relatively high melting points because the formation of oily droplets is promoted through the reciprocal despression in melting point.

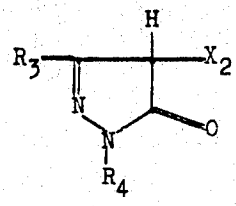
The high boiling crystalloid solvents listed in the following, for example, have proved to be particularly suitable high boiling coupler solvents, i.e., oil formers; ethyl benzyl malonate, phthalic acid dialkyl esters such as dimethyl phthalate, diethyl phthalate, dipropylphthalate, dibutylphthalate, di-n-amyl phthalate and diisoamyl phthalate, dibenzyl phthalate, butyl-o-methoxy benzoate, n-hexyl benzoate, 1,3-diacetoxy benzene, phosphoric acid triaryl esters such as triphenyl phosphate, tricresyl phosphate, tri-p-tert.-butyl phosphate and tri-o-phenyl phenylphosphate, N-butyl acetanilide, acetyl methyl-p-toluidine, benzoyl piperidine, N-n-amyl phthalimide, N-n-amyl succinimide, ethyl-N-phenyl carbamate, N,N-dimethyl-p-toluene sulfonamide, N,N-dibutyl-p-toluene sulfonamide, N,N-di-n-butyl urea, N,N'-diethyl-N,N'-diphenyl urea, benzophenone, 2,4-dichlorobenzophenone, acetophenone, cyclohexanone, n-sec.-amyl-benzophenone, methyl isobutyl ketone, 1-phenyl-1-hydroxy-n-heptane, dibenzyl acetic acid, phenylethyl acetic acid, β-phenylpropionic acid, undecylenic acid, monobenzyl succinate, p-sec.-amyl benzoic acid and mono-n-amylphthalate.

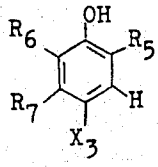
Examples of oil-formers which have also proved to be eminently suitable for the purposes of the invention, include phosphoric acid triaryl esters, especially tricresyl phosphate and phthalic acid dialkyl esters such as di-n-butyl phthalate. There may also be used a number of compounds which by virtue of the different functional groups present in them behave differently in regard to their affinity for the couplers to be dissolved and for the reagents used in the different photographic treatment baths, especially the developer oxidation product. In this way, any average expert is able by choosing a suitable high boiling coupler solvent to adapt the more reactive coupler to the less reactive coupler to meet the particular requirements in regard to coupling velocity. In some cases, the oilformer can be omitted altogether, in which case it is quite sufficient to disperse the colorless coupler, dissolved in a low boiling solvent, in the emulsion whilst the colored coupler is added in an aqueous-alkaline solution.

The colorless couplers according to the present invention are the usual photographic color-forming couplers, i.e., for example open-chain ketomethylene compounds as yellow-forming couplers, 5-pyrazolone derivatives as magenta-forming couplers and phenol or α-naphthol derivatives as cyan-forming couplers. The coupling sites or positions in the coupler molecules are known. Thus ketonmethylene couplers couples to the methylene group activated by an adjacent keto group, pyrazolone couplers couple in the 4-position of the pyrazolone ring whilst phenol and α-naphthol couplers couple in the p-position to the hydroxy group. The colored masking couplers are derived from the colorless couplers in that they contain in the coupling position a substituent which gives the coupler its color and which is eliminated with chromogenic development.

The colorless and colored couplers used to produce the color photographic materials according to the invention consist for example of couplers corresponding to the following formulae I to III:

I 

II 

III 

in which R_1 to R_7 and X_1, X_2 and X_3 represent substituents of the kind that normally occur in colorless and colored photographic color-forming couplers.

More particularly, the symbols R_1 to R_7 and X_1 to X_3 can have the following meanings for example:

R_1 and

R_4 represent an optionally substituted alkyl radical with up to 22 carbon atoms, an aryl radical, preferably a phenyl or naphthyl radical or a heterocyclic radical, preferably a 5- or 6-membered heterocyclic radical containing at least one oxygen, sulphur or nitrogen atom in the ring;

R_2 represents a carbamyl radical which can be substituted on the nitrogen atom for example by aryl radicals such as phenyl radicals or by heterocyclic radicals, or the nitrile group;

R_3 represents an optionally substituted alkyl radical with 6 to 22 carbon atoms or an amino group which can be substituted by alkyl-, aryl- or acyl radicals;

R_5 is a radical with the same meanings as R_1 and may also be a hydrogen atom or a halogen atom or an amino, carbamido, sulfonamido, sulfamyl, carbamyl or alkoxy radical, preferably a carbamyl radical which can be further substituted on the nitrogen, for example, by an alkyl radical with up to 22 carbon atoms, an aryl radical such as a phenyl radical or in which the nitrogen atom is part of a heteroxyclic radical;

R_6 and

R_7 each represent a radical with the same meaning as R_5, also R_6 and R_7 together can form the atoms required to complete a condensed, optionally substituted isocyclic or heterocyclic ring; and

X_1, X_2 and X_3

a) in the case of colorless couplers: represent hydrogen or another non-chromophoric substituent which can be eliminated during color coupling, for example a halogen such as fluorine, chlorine or bromine, a thiocyanogen radical, an alkoxy or aroxy radical, an alkylthio- or arylthio radical, an acyloxy radical, a carboxyl group or a sulfo group,

b) in the case of colored masking couplers; a chromophoric substituent, for example an isocyclic or heterocyclic aromatic radical which is attached through an azo group and which can be further substituted.

The couplers used in accordance with the invention, the colorless as well as the colored couplers, have to satisfy the requirements normally made of them in color photography in regard to resistance to diffusion. This means that they have to be provided with radicals which make them resistant to diffusion, thus preventing them from diffusing undesirably into other layers. Accordingly, useful couplers contain at least one relatively long alkyl radical with from 6 to 22 carbon atoms.

Colorless and colored couplers can also contain groups which render them soluble in aqueous-alkaline solutions, for example carboxyl groups, sulfo groups or sulfonamido groups, although it has proved to be of advantage for the coupler to be dissolved in the oilformers to be more hydrophobic, i.e. if possible not to contain any solubilizing groups.

The following couplers for example have proved to be suitable for use in the preparation of the material according to the invention:

YELLOW-FORMING COUPLERS

1. α-(4-methoxybenzoyl)-2-(N-methyl-N-octadecylamino)-5-(N-methylsulfamyl)-acetanilide
2. α-(2-fluorobenzyl)-2-[(1'-octadecyl-5'-sulfobenzimidazol-2'-yl)-methoxy]-acetanilide
3. α-(3-stearoylaminobenzoyl)-4-(1'-ethoxypropyl-5'-sulfobenzimidazol-2'-yl)-acetanilide
4. α-benzoyl-2-methoxy-5-[N-(2'-methoxy-5'-N-octadecylsulfamylphenyl)-sulfamyl]-acetanilide
5. α-(3-sulfo-4-methoxybenzoyl)-2-(N-methyl-N-octadecylamino-5-(N-butylsulfamyl)-acetanilide
6. α-[2-(1',1',2'-trifluoro-2'-chloroethoxy)-benzoyl]-2-hexadecoxy-5-carboxy acetanilide
7. α-[α'-(2,6-dichlorophenoxy)-isobutyryl]-acetanilide.

Other suitable yellow couplers are described for example in German Patent Specifications . . . (Offenlegungsschriften 1,522,414, 1,522,411, 1,522,412, 1,522,413; Patent Applications P 15 97 464.8, P 19 35 911.6 and P 19 56 281.3).

COLORLESS MAGENTA-FORMING COUPLERS

8. 1-[3'-(2''-chlorobenzyloxy)-4'-methoxy]-3-(α-sulfohexadecanoylamino)-5-pyrazolone
9. 1-[N-(2'-dodecoxyphenyl)-carbamylmethyl]-3-(2'-sulfobenzoyl-amino)-5-pyrazolone
10. 1-(2'-chlor-4'-hexadecylsulfonyl)-3-(2'-sulfobenzoyl)-amino)-5-pyrazolone
11. 1-[2'-(1'',1'',2''-trifluor-2''-chloroethoxy)-phenyl]-3-eikosanoylamino-5-pyrazolone
12. 1-(4'-hexadecylsulfonylphenyl)-3-(2',4',6'-trimethylphenyl sulfonylamino)-5-pyrazolone
13. 1-(4'-difluormethylsulfonylphenyl)-3-(2'-carboxy-5'-hexadecoxy-5-pyrazolone

Other suitable colorless magenta-forming couplers are described for example in German Patent Specifications . . . (Offenlegungsschriften 1,522,434; Patent Applications P 16 22 922.4, P 19 16 869.5, P 19 30 337.8, P 19 31 058.8 and P 19 27 924.4).

COLORED MAGENTA-FORMING COUPLERS

14. 1-(2'-hexadecylthiophenyl)-3-(2'-sulfobenzoylamino)-4-(4'-methoxyphenylazo)-5-pyrazolone
15. 1-(2'-hexadecoxy-5'-chlorphenyl)-3-benzoylamino-4-(2'-methoxyphenylazo)-5-pyrazolone
16. 1-(3'-sulfo-4'-ethoxyphenyl)-3-stearylamino-4-(3'-chlor-4'-methoxyphenylazo)-5-pyrazolone

17. 1-(2'-hexadecylthiophenyl)-3-(2'-sulfobenzoylamino)-4-(4'-sulfopropoxy-phenylazo)-5-pyrazolone
18. 1-(2'-hexadecylthiophenyl)-3-(2'-sulfobenzoylamino)-4-(3'-acetamino-4'-methoxy-phenylazo)-5-pyrazolone
19. 1-(3'-sulfo-4'-phenoxyphenyl)-3-stearoylamino-4-(4'-sulfobutyloxyphenylazo)-5-pyrazolone
20. 1-(4'-phenoxyphenyl)-3-[ω-(2'-tetradecyl-4'-chlor-5'-methylphenoxy)-ethoxycarbonylamino]-4-(4'-sulfopropoxyphenylazo)-5-pyrazolone

Other suitable colored magenta-forming couplers are described for example in German Patent Specifications . . . (Offenlegungsschriften 1,522,436 and 1,522,437).

COLORLESS CYAN-FORMING COUPLERS

21. 1-hydroxy-4-sulfo-N-[ω-N'-phenyl-N'-(N''-octadecylcarbamyl)-aminopropyl]-2-naphthamide
22. 1-hydroxy-N-[ω-N'-phenyl-N'-(2'-tetradecyl-4'-chlor-5'-methylphenoxycarbonyl)-aminopropyl]-2-naphthamide
23. 1-hydroxy-2'-5'-dimethoxy-4'-[4''(α,α, α, α, tetramethylbutylphenoxy)-ethoxycarbonylamino]-2-naphthanilide
24. 1-hydroxy-5,6,7,8-tetrahydro-2'-5'-dimethoxy-4'-[4''-(α,α,α-trimethylpentylphenoxy)-ethoxycarbonylamino]2-naphthanilide
25. 1-hydroxy-2'-fluoro-5'-(N-methyl-N-hexadecylsulfamyl)-2-naphthanilide
26. 2,4-dichlor-3-methyl-6-(2'-chlor-5'-pentadecyl-phenoxy)-acetamino)-phenol
28. 1-hydroxy-N-[4'-(N'-methyl-N'-octadecyl-sulfamyl)-phenoxyethyl]-2-naphtamide
29. 1-hydroxy-N-[4'-(N'-ethyl-N'-cyclohexylsulfamyl)-phenobutyl]-2-naphthamide
30. 1-hydroxy-N-(N'-β,β-dimethyleikosoxycarbonylindolin 6'-yl)-2-napthamide

Other suitable colorless cyan-forming couplers are described, for example, in German Patent Specification . . . (Offenlegungsschrift 1,522,416; Patent Applications P 16 22 920.2, P 15 22 402.9, P 19 15 948.9, P 19 44 440.7 and P 19 22 628.9).

COLORED CYAN-FORMING COUPLERS

31. 1-hydroxy-4-(2'-acetylphenylazo)-N-[N'-(4'-ethoxyphenyl-N'-(N''-octadecylcarbamyl)-aminoethyl]-2-naphtamide
32. 1-hydroxy-4-(2'-sulfophenylazo)-N-[-N'-(2-ethoxyphenyl)-N'-(N''-octadecylcarbamyl)-aminopropyl]-2-naphthamide
33. 1-hydroxy-4-(2'-sulfo-5'-acetaminophenylazo)-2'-(N-methyl-N-octadecylamino)-5'-sulfo-2-naphthanilide
34. 1-hydroxy-4-(2'-sulfo-4'-6'-dichlorophenylazo)-2'-hexadecoxy-5'-carboxy-2-naphthanilide
35. 1-hydroxy-4-(3',5'-dicarboxyphenylazo)-2'-(N-methyl-N-octadecylamino)-5'-methylsulfamyl-2-naphthanilide
36. 1-hyroxy-4-(2',4'-disulfophenylazo)-2'-(N-methyl-N-octadecylamino)-5'-sulfo-2-naphthanilide

Other suitable colored cyan-forming couplers are described, for example, in German Patent Specification . . . (Offenlegungsschrift 1,522,422; Patent Applications P 15 97 510.7 and P 19 44 441.8).

In connection with the yellow-forming, magenta-forming and cyan-forming couplers to be used, reference is also made to the article by W. Pelz in "Mitteilungen aus den Forschungslaboratorien der Agfa" Leverkusen-Muenchen, Vol.III, page 111 (Springer-Verlag Berlin, Goettingen, Heidelberg, 1961).

Suitable photosensitive emulsions include emulsions of silver halides such as silver chloride, silver bromide or mixtures thereof, optionally containing small quantities of silver iodide of up to 10 mol per cent in one of the hydrophilic binders normally used such as protein, especially gelatin, polyvinyl alcohol, polyvinyl pyrrolidone, cellulose derivatives such as carboxyalkyl cellulose, especially carboxymethyl cellulose or derivatives of alginic acid.

The emulsions may also contain the usual additives, for example spectral or chemical sensitizers, stabilizers, hardeners and plasticisers.

Any color-forming developers containing a primary amino group can be used for development. Developers of the p-phenylene diamine type are preferred, for example N,N-dimethyl-p-phenylene diamine, N,N-diethyl-p-phenylene diamine, monomethyl-p-phenylene diamine, 2-amino-5-diethylamino toluene, N-butyl-N-ω-sulfobutyl-p-phenylene diamine and 2-amino-5-(N-ethyl-N-β-methane sulfonamido ethylamino)-toluene.

EXAMPLES

1 kg of a red-sensitized photographic silver bromide emulsion containing 95 g of gelatin and 0.4 mol of silver bromide, is used in each of the following Examples unless otherwise stated. This emulsion then has the couplers added to it either in aqueous-alkaline solution, optionally with methanol added, or in the form of a dispersion in gelatin solution. This is followed by the addition of 25 ml of 1 percent solution in methanol of 4-hydroxy-6-methyl-1,3,3a,7-tetra azaindene, 30 ml of a 10 percent aqueous saponin solution and 15 ml of a 0.5 percent aqueous chromium acetate solution. The product is then adjusted to pH 6.7, cast on to a layer substrate of cellulose triacetate and dried. The dried layer is from 3.8 to 4.5 μ thick.

The coupler dispersions are prepared as follows:

20 g of coupler are dissolved in 60 ml of ethyl acetate and the resulting solution emulsified in 320 ml of a 10 percent aqueous gelatin solution to which 11 ml of a 10 percent aqueous saponin solution has been added. Where oil-formers are used, the 60 ml of ethyl acetate are replaced by a mixture of 20 ml of the oilformer and 40 ml of ethyl acetate.

After drying, the material is exposed through a continuous grey wedge, developed in a colorforming developer bath and then further processed as follows:

STOPPER BATH - 4 MINUTES

17 ml of glacial acetic acid
2.94 g of anhydron-sodium acetate
made up to 1 litre with water

HARDENING BATH - 4 MINUTES

0.3 g of sodium hydroxide
0.5 g of sodium hexamethaphosphate
9.04 g of sodium carbonate
20 ml of 37 percent aqueous formalin
made up to 1 litre with water

BATHING IN WATER - 5 MINUTES

BLEACHING BATH - 6 MINUTES

6 g of sodium hexametaphosphate

42.0 g of potassium ferricyanide
12.0 g of potassium bromide
6.0 g of disodium phosphate
16.0 g of mono potassium phosphate
made up to 1 litre with water

BATHING IN WATER - 5 MINUTES

FIXING BATH - 8 MINUTES

150 g of ammonium thiosulfate
10 g of sodium sulfite
made up to 1 litre with water

BATHING IN WATER - 10 MINUTES

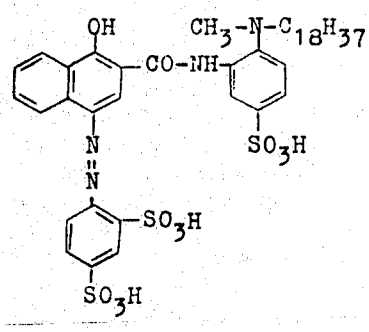
FINAL BATH - 30 SECONDS

0.3 g of sodium tetrapropylene benzene sulfonate
made up to 1 l with water

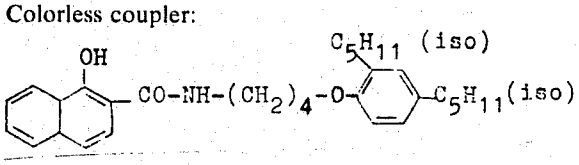
The density of the color wedges obtained is then measured behind blue, green and red filters. In FIGS. **4** to **13**, curve 1 represents the cyan-green density, curve 2 the magenta density and curve 3 the yellow density, in each case in dependence upon exposure.

EXAMPLE 1

Masking coupler:



Colorless coupler:



Three different materials (A, B and C) were prepared. In each case, 120 ml of a 5 percent solution of the masking coupler in dilute sodium hydroxide was added to the emulsion, together with 200 ml of one of the following dispersions of the colorless coupler:

A: no oilformer
B: oilformer: dibutyl phthalate
C: oilformer: tricresyl phosphate

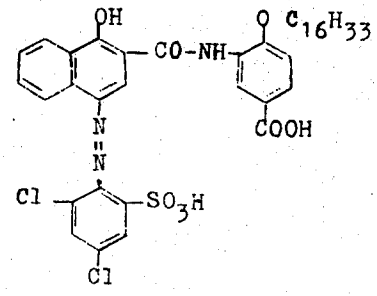
The dried materials are developed for 15 minutes in a color-forming developer of the following composition and then further processed as just described:

5 g of 2-amino-5-(N-ethyl-N-β-methanesulfonamidoethylamino)-toluene-sesquisulfate monohydrate
5 ml of benzyl alcohol
2.5 g of sodium hexamethaphosphate
1.85 g of anhydrous sodium sulfite
1.4 g of sodium bromide
0.5 mg of potassium iodide
12.5 g of sodium hydroxide
34.22 g of $Na_2B_4O_7.5H_2O$
made up to 1 litre with water

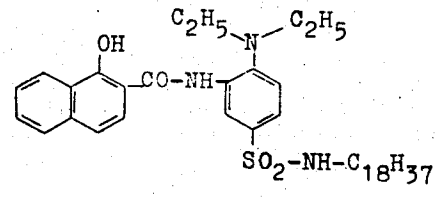
The results are set out in FIGS. **4** (material A), 5 (material B) and 6 (material C). Whereas in the case of material A the curve of the magenta side density of the cyan dye formed from the coupler shows a distinct hump, straight lines are obtained for the side densities in the case of materials B and C. The materials B and C are much better masked.

EXAMPLE 2

Masking coupler:



Colorless coupler:



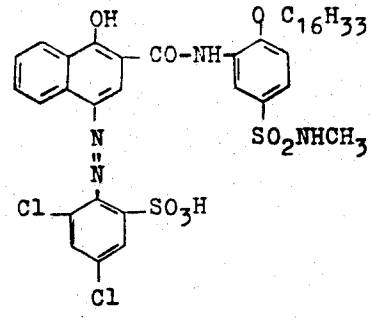
Three different materials, (A, B and C) were prepared, 135 ml of a 5 percent solution of the masking coupler in a dilute lithium hydroxide solution was added to the emulsion in each case, followed by the addition of 15 g of the colorless coupler in the following manner:

A: 300 ml of a 5 percent solution of the colorless coupler in a dilute aqueous methanolic sodium hydroxide solution
B: 300 ml of the coupler dispersion without any oilformers,
C: 300 ml of the coupler dispersion containing dibutyl phthalate as oilformer.

The material is processed as in Example 1.

The results can be seen from FIG. **7** (material A), 8 (material B) and 9 (material C). It is only in material C that the yellow and magenta side densities are adequately masked.

Similar results are obtained by using a masking coupler of the following formula instead of the aforementioned masking coupler:



(145 ml of a 5 percent solution in dilute sodium hydroxide).

EXAMPLE 3

Materials A and C of Example 2 are developed in a developer of the following composition and then further treated in the usual way:

2.5 g of N,N-diethyl-p-phenylene diamine monosulfate
2 g of sodium sulfite
1 g of potassium bromide
75 g of potassium carbonate
0.5 g of hydroxyl amine
made up to 1 litre with water

In this case too material C shows a better masking effect.

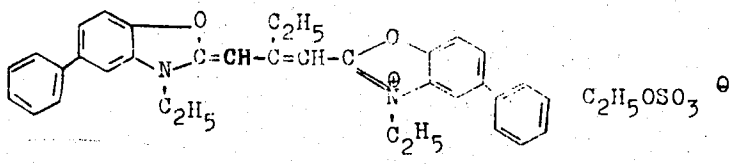
Processing is carried out as in Example 3. The results can be seen from FIGS. **10** (material A) and 11 (material B). The yellow side density is excellently masked in the case of material B.

EXAMPLE 5

Three-layer materials were made up in which the materials A and C of Example 1 are further coated in the following order:

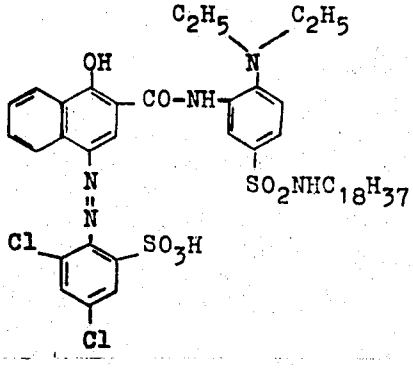
1. gelatin intermediate layer - 2 μ
2. layer containing a magenta-forming coupler - 4.2 μ

A silver bromide emulsion green-sensitized by the addition of 60 ml of a 0.1 percent solution in methanol of the following dye:

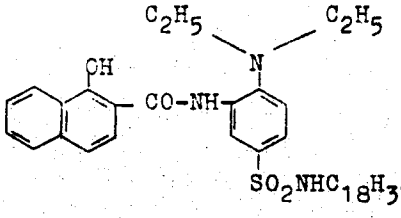


EXAMPLE 4

Masking coupler:



Colorless coupler:



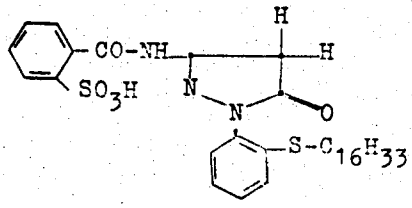
Two materials A and B were prepared, 200 ml of a 5 percent solution of the masking coupler in dilute sodium hydroxide was added to the emulsion in each case, followed by the addition of 14 g of the colorless coupler in the following manner:

A: in the form of a 5 percent methanolic aqueous-alkaline solution,

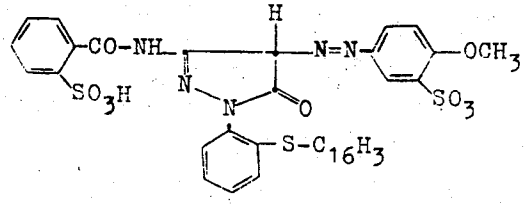
B: in the form of a dispersion using dibutyl phthalate as the oilformer,

has added to it per kg:

240 ml of a 5 percent aqueous-alkaline solution of a colorless coupler corresponding to the formula:



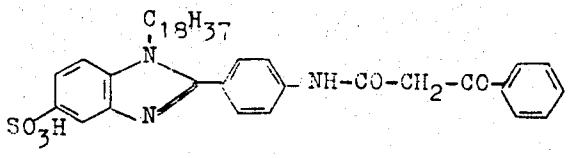
and 120 ml of 5 percent aqueous-alkaline solution of a colored coupler of the formula:



and the usual additives.

3. Gelatin intermediate layer - 1μ
4. Yellow filter layer colloidal silver in 2 percent aqueous gelatin solution (optical density 0.6)
5. A layer containing a yellow coupler - 4.2μ

An unsensitized silver bromide emulsion containing per kg 0.26 mol of silver bromide and 90 g of gelatin, has added to it 500 ml of an aqueous-alkaline solution of a yellow-forming coupler of the formula:



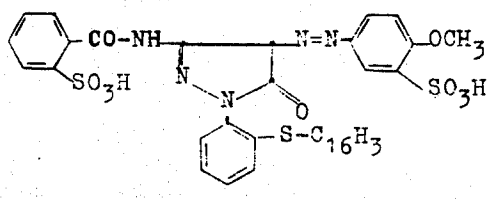
and the usual additives.

6. Gelatin protective layer - 1μ

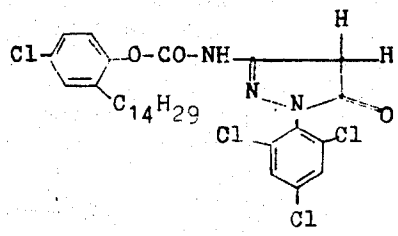
The material is processed as in Example 1. It was found that the three-layer material obtained from A is inadequately masked whilst satisfactorily compensated, gradationfree yellow and magenta side densities are obtained in the case of the material obtained from C.

EXAMPLE 6

Masking coupler:



Colorless coupler:



Two materials A and B were made up, the silver bromide emulsion having added to it in each case 130 ml of a 5 percent aqueous-alkaline solution of the masking coupler and 12 g of the colorless coupler:

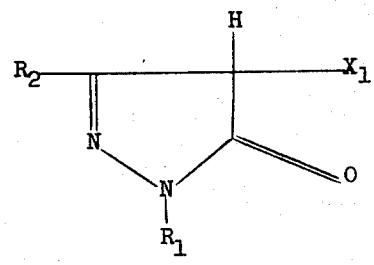
A: in the form of a 5 percent aqueous-alkaline solution,

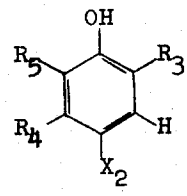
B: in the form of a dispersion using dibutyl phthalate as the oilformer.

In this case, too, material B (FIG. 13) is excellently masked, whilst material A (FIG. 12) shows an irregular yellow side density.

What is claimed is:

1. A color photographic multiple-layer material containing colorforming couplers and comprising at least one red-sensitized, one green-sensitized and one blue-sensitive silver halide emulsion layer and dispersed in at least one of the first two layers a less reactive colored masking coupler and a more reactive colorless coupler, wherein the improvement comprises (1) at least one of the first two layers consisting partly of an oil former having a boiling point of at least 175°C distributed in said layer and containing the more reactive colorless coupler dissolved in the oil former, and (2) the less reactive colored masking coupler is contained in the non-oil former part of said layer, both couplers containing at least one long alkyl radical with 6–22 carbon atoms in a non-coupling position on the coupler, said group making said couplers non-diffusible to produce upon color development dyes of substantially the same color that remain in the layer and contribute to the same partial image, the colored coupler being selected from the group consisting of

I 

II 

in which

R_1 represents an alkyl radical with up to 22 carbon atoms or an aryl radical or a heterocyclic radical containing at least one oxygen, sulfur or nitrogen atom in the ring;

R_2 represents an alkyl radical with up to 22 carbon atoms or an amino group substituted by an alkyl-, aryl- or acyl radical;

R_3 is an amino, carbamido, sulfonamido, sulfamyl or carbamyl radical;

R_3 and at least one of R_1 and R_2 contain a relatively long alkyl radical with at least 6 carbon atoms;

R_4 and R_5 each represent a hydrogen atom, a halogen atom or an alkyl radical, or R_5 and R_4 together form the atoms required to complete a condensed, isocyclic or heterocyclic ring; and

X_1 and X_2 represent as a chromophoric substituent, an isocyclic or heterocyclic aromatic radical which is attached through an azo group,

whereby the coupling reaction of the more reactive colorless coupler is delayed with respect to the coupling reaction of the less reactive colored coupler.

2. In the color photographic multiple-layer material as claimed in claim 1 the oil former selected from the group consisting of phosphoric acid triaryl ester and phthalic acid dialkyl esters.

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