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SENSITIZED COLOR PHOTOGRAPHIC EMULSIONS AND PROCESSES CONTAINING COLOR COUPLERS

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9 Claims. (Cl. 96—100)

This application is a continuation-in-part application of copending United States application Serial No. 131,929, filed August 16, 1961.

This invention concerns improvements in or relating to color photographic emulsions and processes.

More particularly it relates to the preparation of color-responsive silver halide emulsions suitable for use in the production of single- or more usually multi-layer color photographic media, which upon exposure and development in the appropriate manner will yield either a negative or positive color image, according to principles and techniques in themselves now well known.

In the preparation of color-responsive silver halide emulsions it is conventional to incorporate in the emulsion destined to form any given layer not only silver halide and a so-called sensitizer capable of enhancing the photo-sensitiveness of the silver halide to those wavelengths of light to which that layer is intended to respond, but also a so-called color coupler whose function is to react with the oxidation product of the developer to form a dye of the appropriate color. Where multi-layer color photographic media are intended to be built up by superimposing differently sensitized layers upon a film base or other support it is obviously necessary to ensure that the color couplers incorporated in any one layer do not diffuse or otherwise migrate into the adjacent layer or layers.

Two fundamentally different approaches have hitherto been adopted therefore in the preparation of color-responsive silver halide emulsions intended primarily for the production of multi-layer photographic media, but which it will of course be understood may equally serve for the production of single layers.

In one approach to the problem of securing a sensitized silver halide emulsion containing a diffusion-resistant color coupler, which for convenience will hereinafter be referred to as "process I" and which is typified by color film sold under the name "Agfacolor," the compounds employed as the color couplers are soluble in water, achieved by the substitution of sulfo- or carboxyl-groups into the molecule, but their diffusion resistance is ensured by the presence of a long aliphatic hydrocarbon chain in the molecule, as described for instance in German Patent 726,611. In the preparation of the emulsion these water-soluble compounds are merely dissolved in dilute sodium hydroxide solution and thereupon added to and thoroughly mixed with the silver halide emulsion.

The other approach to the problem, which for convenience will hereinafter be referred to as "process II" and which is typified by color film sold under the name "Ektachrome," involves the use as color couplers of compounds which are insoluble in water. In order to incorporate these water-insoluble color couplers in the silver halide emulsion it is however necessary to proceed in the manner which has been described in United States Patent 2,322,027, according to which the color coupler is first made up into a solution with a so-called oil former, usually a high-boiling point solvent insoluble in water, and this oily solution is then dispersed in droplets through-

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out an aqueous gelatin solution, and finally the dispersion thus prepared is mixed with the silver halide emulsion. In this process the need for inherent diffusion-resistance of the color couplers themselves is greatly reduced, since their water-insolubility and their dispersion in conjunction with the oil former combine to impart a measure of protection against diffusion.

With both of these known types of process it is of course quite possible to achieve satisfactory results, but nevertheless both process I and process II have their disadvantages. In process I these stem primarily from the surface active effects of the color couplers, which are soap-like in character and consequently exert a strong influence upon the viscosity of the prepared emulsion, giving rise to difficulties during the coating procedure. In process II the disadvantages are attendant upon the use of oil-formers, whose presence in the form of distribution of oily droplets lends an undesired moistness to the finished emulsion-layer and can moreover give rise to color fogging during the development process.

Attempts have been made to find a process which avoids the disadvantages both of process I, due to the presence of solubilizing groups in the coupler molecule, and also those of process II, due to the use of an oil former. Color couplers have in fact already been described, in for example German Patent 725,872, which as a result of the presence of a long aliphatic hydrocarbon chain are diffusion-resistant, and which, since they contain no sulfo- or carboxyl-groups, are practically insoluble in water. It is moreover feasible to produce fine dispersions of such color couplers without the use of an oil former by dissolving them in a low-boiling point water-immiscible solvent and dispersing this solution with the aid of a wetting agent in an aqueous gelatin solution. The low-boiling point solvent can then be removed immediately, for example by evaporation, or removal can take place subsequently, after mixing of the dispersion with the silver halide emulsion, upon drying of the finished layer of emulsion formed in the coating procedure. Development of such a finished layer with a conventional color developer gives a clear and intense color image; but unfortunately other unexpected difficulties arise when an attempt is made to build up photographic media on the basis of emulsions containing such coupler dispersions, inasmuch as the usual sensitizers employed in such emulsions have been found to be incompatible in the silver halide emulsion with coupler dispersions of this kind.

It has in fact been established that the majority of the dyes hitherto proposed for use as photo-sensitizers for silver halide are unsuitable for use in conjunction with this kind of coupler dispersion. Their unsuitability demonstrates itself in practice in terms of a decline from hour to hour of the spectral sensitivity of such an emulsion upon standing. As a result a coating procedure of long duration, and even exceeding several seconds, becomes impractical, and moreover a generally similar decline in the spectral sensitivity is encountered upon storage of the finished layer. This rather surprising state of affairs can presumably be accounted for by the hypothesis that in this process the sensitizer is displaced from the silver halide surface by the color coupler whereas in processes I and II, respectively, the water-solubility of the coupler in the one case and the presence of the oil former in the other case prevent the coupler from competing with the sensitizer for adsorption onto the silver halide grains.

It is an object of the present invention to provide color photographic emulsions and processes which largely or wholly avoid the disadvantages of all these known procedures, and this is achieved by a careful selection of certain types of color coupler for use with certain types of sensitizer.

It has in fact now been found:

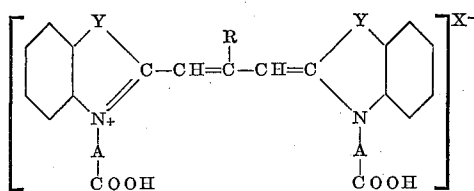
(1) That for the production of the cyan image it is possible to use phenolic color couplers whose molecule contains a long carbon chain with from 10 to 21 carbon atoms but no acid groups, since these in the absence of an oil former are fully compatible in a silver halide emulsion with red sensitizers provided that the latter are chosen from the class of *ms*-alkyl-benzthio- or -benzseleno-carbocyanines whose two ring nitrogen atoms are substituted by carboxy-alkyl groups.

(2) That for the production of the magenta image it is possible to use pyrazolone color couplers whose molecule contains a long carbon chain with from 10 to 21 carbon atoms but no acid groups, since these in the absence of an oil former are fully compatible in a silver halide emulsion with green sensitizers provided that the latter are chosen from the class of benzthio- or -benzseleno-pseudocyanines in which one ring nitrogen atom is substituted by a carboxyl-alkyl group.

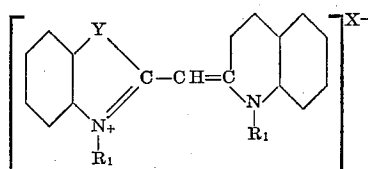
Using these combinations of a type of coupler known per se with a type of sensitizer known per se, stable emulsions can be prepared from which single- or multi-layer color photographic media can be built up, and since no acid groups are present in the coupler molecule and the use of oil formers is unnecessary the previously-explained disadvantages of both processes I and II are avoided. The procedure used according to this invention in fact gives highly satisfactory results contrary to expectation in the light of knowledge about the liability for a decline of spectral sensitivity in the absence of an oil former and surprising insofar as they were not predictable from the individual properties of the respective selected classes of coupler and sensitizer. Emulsions prepared in accordance with this invention are easy and safe to handle during the coating operation, and the layers formed from them do not display the disadvantages which are observed upon use of oil formers. In particular the total volume of the finished emulsion is somewhat reduced and the dye image ultimately formed is highly stable, while the finished layer displays an outstanding resistance to abrasion or other mechanical damage as compared with the known layers containing oil formers.

The dyes which are used as the sensitizers according to the invention have the following general formula:

RED SENSITIZERS



GREEN SENSITIZERS



In the two general formulas shown above Y represents sulphur or selenium, R represents an alkyl group, A represents an alkylene group, one R₁ is a lower alkyl radical and the other R₁ —A—COOH and X represents an anion, while the benzene nucleus can bear any of the usual substituents, such as alkyl, alkoxy, naphthyl groups, halogen atoms and so on. The most diverse anions may be employed, including inter alia the following, namely halogen anions such as chloride, bromide and iodine, also perchlorate, sulphate, monoalkylsulphate, acetate and the like. Instead of the salt form

shown these dyes can in fact also be employed in the form of the corresponding betaine.

It will be observed that all the sensitizers to be used according to this invention have as a common characteristic a carboxy-alkyl group in the molecule. Dyes possessing this characteristic are in fact already known, having been described for example in German Patent No. 704,141 and indeed they are known to be suitable for use in conjunction with color couplers in silver halide emulsions. Whereas however it is possible, using these sensitizers or indeed many others to produce stable combinations of sensitizer—color coupler—silver halide when the procedures of the aforesaid processes I or II are employed, with of course the attendant disadvantages which have been previously described, what has hitherto never been recognized is that only by the selection of these sensitizers characterized by the presence of the carboxy-alkyl substituent, for use in conjunction with the classes of color coupler selected in accordance with this invention, does it become possible to achieve, in the absence of an oil former, results which in general are satisfactory and in particular are free from the disadvantages previously specified herein.

Color couplers suitable for forming the cyan or blue-green image according to the invention are derivatives of phenol or α -naphthol having a long aliphatic hydrocarbon residue in the molecule. The carbon chain should be sufficiently long in order to arrest diffusion completely, and to this end in general a chain length of over 10 carbon atoms is needed: the optimum chain length in any particular circumstances can easily be determined by tests. In most cases the preferred couplers are those in which the chain consists of 17 or 18 carbon atoms. Such phenol or α -naphthol derivatives per se are known, as well as methods of preparing them, and need not be further described herein. It should be noted that, provided the carbon chain contains from 10 to 21 carbon atoms, it is immaterial whether it is straight- or branched-chain and it may be an unsubstituted hydrocarbon chain or if desired can bear any of the usual substituents, such as aryl-, alkoxy- or aryloxy- groups.

Merely by way of illustration the following compounds are listed as examples of cyan color couplers suitable for use in accordance with the present invention:

- 5-stearoylamino-1-naphthol
- 1-hydroxy-2-naphthoic acid (4'-octadecyloxy)-anilide
- N,N'-dodecamethylene-bis-(1-hydroxy-2-naphthylamide)
- 1-hydroxy-2-naphthoic acid octadecylamide
- 1-hydroxy-4-bromo-naphthoic acid octadecylamide
- 1-hydroxy-4-chloronaphthoic acid octadecylamide
- 1-hydroxy-4-bromo-naphthoic acid hexadecylamide
- 1-hydroxy-4-chloro-naphthoic acid hexadecylamide
- 1-hydroxy-2-naphthoic acid N-octadecyl-anilide
- 1-hydroxy-2-naphthoic acid dodecyloxy-butylamide
- 2,4-dichloro-5-stearoylamino-1-naphthol
- 2-palmitoylamino-4-chloro-5-methyl-phenol
- 2-octadecyl-4-chloro-phenol

As regards the pyrazolone color couplers to be used according to the present invention for forming the magenta image the same remarks concerning the length and nature of the aliphatic chain hold good as in the case of those employed to form the cyan image. Again, merely as illustration, the following compounds are listed as examples of suitable magenta color couplers:

- 1-phenyl-3-heptadecyl-pyrazolone-5
- 1-phenyl-3-stearoylamino-pyrazolone-5
- 1-(2'-benzthiazolyl)-3-dodecyl-pyrazolone-5
- 1-phenyl-3-pentadecyl-pyrazolone-5
- 1-(2'-aminophenyl)-3-heptadecyl-pyrazolone-5
- 1-(4'-bromophenyl)-3-pentadecyl-pyrazolone-5
- 1-(2',4'-dichlorophenyl)-3-heneicosyl-pyrazolone-5

1-(2',4',6'-trichlorophenyl)-3-stearoylamino-pyrazolone-5
1-(2',4',6'-trichlorophenyl)-3-heptadecylamino-pyrazolone-5

The dispersion of the color coupler must not be effected with the aid of oil formers such as those which are used, for example, in the process of U.S. Patents 2,304,940 and 2,322,027 because they have the disadvantages mentioned above in the specification.

The dispersion of the color coupler is instead effected according to methods well known to those skilled in the art in order to distribute water-insoluble substances as finely as possible in aqueous media. Thus, for instance, the color couplers may be dispersed in low boiling point, water immiscible solvents such as ethyl acetate, propyl acetate, methyl propionate, chloroform, nitroethane, nitromethane and the like, which are removed again from the emulsion in the course of the process.

However, the desired dispersions may also be obtained by finely milling the coupler substances in a colloid mill.

Another method for effecting the dispersion consists of stirring the couplers in the presence of a strong alkali and of a known wetting agent with the gelatin solution, whereupon the gelatin solution is subsequently neutralized by the addition of an acid. In all instances a very fine dispersion is obtained which dries completely transparent after pouring it onto a photographic film carrier.

The red-sensitizers which are to be used according to the invention in combination with the specified phenolic cyan couplers should possess a narrowly limited spectral sensitization band at the red end of the spectrum, and this requirement is apparently best achieved by choosing ethyl residue as the alkyl substituent in the *ms*-position (see the above general formula). While other carboxy-alkyl groups are suitable as the nitrogen substituent a β -carboxy-ethyl group is preferably employed. Illustrative examples of suitable red sensitizer dyes are shown in the following list:

1,1-di-(β -carboxy-ethyl)-5,6,5',6'-tetramethyl-9-ethyl-benzthio-carbocyanine iodide
1,1'-di-(β -carboxy-ethyl)-6,6'-dichloro-9-ethyl-benzthio-carbocyanine iodide
1,1'-di-(β -carboxy-ethyl)-6,6'-dimethoxy-9-ethyl-benzthio-carbocyanine iodide
1,1'-di-(γ -carboxy-propyl)-5,6,5',6'-tetramethyl-9-ethyl-benzthio-carbocyanine iodide
1,1'-di-(γ -carboxy-propyl)-6,6'-dichloro-9-ethyl-benzthio-carbocyanine iodide
1,1'-di-(γ -carboxy-propyl)-6,6'-dimethoxy-9-ethyl-benzthio-carbocyanine bromide
1,1'-di-(γ -carboxy-ethyl)-5,5'-dimethoxy-6,6'-dimethyl-9-ethylbenzthio-carbocyanine iodide
1,1'-di-(β -carboxyethyl)-6,6'-dichloro-9-ethyl-benzthio-carboxycyanine iodide

The green-sensitizers which are to be used according to the invention in combination with the specified pyrazolone magenta couplers may for example include the following:

1-(β -carboxy-ethyl)-1'-ethyl-6,6'-dimethoxy-benzthio-pseudocyanine iodide
1-(β -carboxy-ethyl)-1'-ethyl-6-phenyl-6'-methoxy-benzthio-pseudocyanine bromide
1-(β -carboxy-ethyl)-1'-ethyl-5-methyl-6,6'-dimethoxy-benzthio-pseudocyanine iodide
1-(β -carboxy-ethyl)-1'-ethyl-4,5-naphtho-pseudocyanine bromide

It will of course be understood that, as regards the sensitization effect, it is in every respect a matter of indifference whether the dye salt or the corresponding betaine is employed, and that, as regards the dyes themselves, these may be obtained in accordance with known methods.

In order that the invention may be well understood the following illustrative examples will now be given:

Example 1.—Production of a silver halide emulsion for the cyan image

1 kg. of a silver bromide emulsion prepared in the usual way is sensitized with 30 mg. of 1,1'-di-(β -carboxy-ethyl)-6,6'-dimethoxy-9-ethyl-benzthio-carbocyanine, dissolved in ethanol.

A coupler dispersion is then introduced, which is prepared in the following manner: 10 g. of 1-hydroxy-2-naphthoic acid octadecylamide are dissolved in 30 ml. of ethyl acetate with warming, and dispersed in a colloid mill with 160 ml. of 5% gelatin solution which contains 1 g. of dodecylbenzene-sulphonate. The ethyl acetate is then removed from this dispersion by evaporation.

After the mixing of the coupler dispersion with the silver halide emulsion, and introduction of the conventional coating additives the finished emulsion is coated onto a film base in the usual manner and dried.

After exposure through a grey-wedge behind a red filter, development in a dialkyl phenylene diamine developer and bleaching of the silver, an intense clear blue-green wedge is obtained. The same sensitometric data are secured if the finished emulsion has been allowed to stand for several hours before the coating operation. Moreover if the finished layer is subjected to an accelerated storability test, no decline in sensitivity is observed, or at most only a quite insignificant decline.

Substantially similar results may be secured by substituting any of the following couplers, namely 1-hydroxy-2-chloro-naphthoic acid octadecylamide, 1-hydroxy-2-naphthoic acid N-octadecyl-anilide, 1-hydroxy-2-naphthoic acid dodecyloxy-butylamine and 1-hydroxy-2-naphthoic acid octadecylamide, and/or any of the following sensitizers, namely 1,1'-di-(β -carboxy-ethyl)-6,6'-dichloro-9-ethyl-benzthio-carbocyanine iodide, 1,1'-di-(β -carboxy-ethyl)-5,5'-dimethoxy-9-ethyl-benzthio-carbocyanine iodide, 1,1'-di-(β -carboxy-ethyl)-6,6'-dichloro-9-ethyl-benzthio-carbocyanine iodide and 1,1'-di-(β -carboxy-ethyl)-6,6'-dimethoxy-9-ethyl-benzthio-carbocyanine, for the coupler and/or sensitizer, respectively, used in Example 1 above, so as to obtain an excellent emulsion for the cyan image.

Example 2.—Production of an emulsion for the magenta image

The same procedure is adopted as in Example 1, except that the sensitizer there employed is replaced by 30 mg. of 1-(β -carboxy-ethyl)-1'-ethyl-6-phenyl-6'-methoxy-benzthio-pseudocyanine, and the coupler there employed is replaced by 10 g. of 1-phenyl-3-heptadecyl-5-pyrazolone. After coating, exposure, development and so on in the same manner as described in Example 1 a clear intensive magenta is secured. The stability of the finished emulsion prior to coating and the storability of the finished layer are both excellent as in Example 1.

Substantially equivalent results may be secured by substituting any of the following couplers, namely 1-phenyl-3-stearoylamino-pyrazolone-5, 1-(2',4'-dichlorophenyl)-3-heneicosyl-pyrazolone-5, 1-(2',4',6'-trichlorophenyl)-3-heptadecylamino-pyrazolone-5 and 1-phenyl-3-heptadecyl-pyrazolone-5, and/or any of the following sensitizers: namely 1-(β -carboxy-ethyl)-1'-ethyl-6,6'-dimethoxy-benzthio-pseudocyanine iodide, 1-(β -carboxy-ethyl)-1'-ethyl-5-methyl-6,6'-dimethoxy-benzthio-pseudocyanine iodide and 1-(β -carboxy-ethyl)-1'-ethyl-6-phenyl-6'-methoxy-benzthio-pseudocyanine for the coupler and/or sensitizer, respectively, used in Example 2 above, so as thus to yield an excellent emulsion for the magenta image.

Example 3.—Production of a multi-layer film

The emulsion described in Example 1 for the cyan or blue-green image is first coated onto a film base or other support, and then the emulsion described in Example 2 for the magenta image is superimposed upon it. A yellow filter layer which contains colloidal silver or a bleach-

able pigment is then applied, and followed by an unsensitized emulsion layer which contains a dispersed yellow coupler such as for example N-(p-benzoylacetamino-benzenesulphonyl) - N - octadecyl - N - methyl - amine.

If this multi-layer material after exposure is developed in a color developer then, after removal of the silver, a negative color image is obtained. If on the contrary the material after exposure is subjected to the reversal development process, and thus is developed first in, for example, metol-hydroquinone and only afterwards in a color developer then, after removal of the silver, a color positive is obtained. The sensitivity of the material behind green and red-filters is practically the same after storage as in the fresh condition.

Example 4

12 grams of 1-(2',4',6',-trichlorophenyl)-3-hepta-decyl-pyrazolone-5) were dissolved in 40 cc. of hot ethanol, and then 13 cc. of 2 N sodium hydroxide were added and the mixture was diluted with 60 cc. of water at 40° C. The warm solution was admixed with a solution of 10 grams of gelatin and 1.5 grams of sodium dodecylbenzene sulfonate in 100 cc. of water at 40° C. While stirring, the highly viscous gelatin solution was neutralized with 13 cc. of 2 N acetic acid or mineral acid. An extremely fine dispersion was obtained thereby, which dried completely transparent upon pouring. If it is desired to remove the alcohol and salts, the dispersion is allowed to solidify and is washed with water after it has been comminuted. Subsequently the solidified gelatin is melted again and, after admixing it with a silver halide emulsion containing as a green-sensitizer 1-(β-carboxyethyl)-1'-ethyl-6,6'-dimethoxybenzelenopseudocyanin iodide, it is poured into a film carrier and dried. After exposure and development, a clear purple image is obtained.

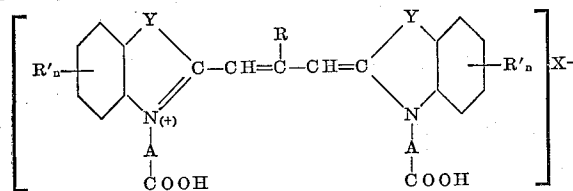
Example 5

200 cc. of a 6% gelatin solution and 20 cc. of 10% sodium alkyl naphthalene sulfonate were heated in a heatable mixer at 80° C. with a mixture consisting of 6 grams of 1-hydroxy-2-naphthoic acid-octadecylamide (M.P. 78° C.) and of 6 grams of 1-hydroxy-2-naphthoic acid-lauryloxypropylamide (M.P. 42° C.) and dispersed at 18,000 r.p.m. After admixing with a silver halide emulsion containing 1,1-di-(β-carboxyethyl)-6,6'-dichloro-9-ethyl-benzelenocarbocyanin iodide as a red sensitizer, the procedure of Example 4 was followed to form a clear blue-green image.

Various modifications of the process of the invention may be made without departing from the spirit or scope thereof and it is to be understood that the invention is to be limited only as defined in the appended claims.

We claim:

1. A process for the preparation of color photographic emulsions for the production of the cyan image which comprises forming a silver halide emulsion sensitized with a compound selected from the group consisting of a compound having the formula



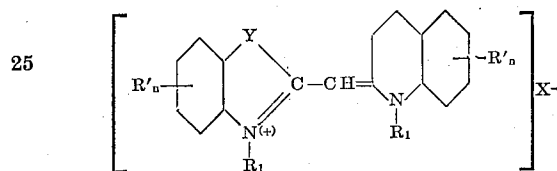
wherein R is a lower alkyl radical, R' is selected from the group consisting of hydrogen, lower alkyl radicals, lower alkoxy radicals, naphthylene and halogen, n is an integer from 1 to 2, A is a lower alkylene radical, Y is selected from the group consisting of selenium and sulfur atoms and X is an anion and its betaine derivatives, forming a dispersion of a color coupler selected from the group consisting of phenols and α-naphthols lacking solubilizing groups and having an aliphatic hydrocarbon residue of

10 to 21 carbon atoms therein in the absence of oil formers and mixing the said silver halide emulsion and the said dispersion to form the desired color photographic emulsions.

2. The process of claim 1 wherein the color coupler is selected from the group consisting of 1-hydroxy-4-chloro-2-naphthoic acid N-octadecylamide, 1-hydroxy-2-naphthoic acid N-octadecylamide, 1-hydroxy-2-naphthoic acid N-dodecyloxybutylamide and 1-hydroxy-2-naphthoic acid N-octadecylamide.

3. The process of claim 1 wherein the sensitizer is selected from the group consisting of 1,1'-di-(β-carboxyethyl) - 6,6' - dichloro-9-ethyl-benzeleno - carbocyanine iodide, 1,1'-di-(β-carboxyethyl) - 5,5' - dimethoxy-9-ethyl-benzthio-carbocyanine iodide, 1,1'-di-(β-carboxyethyl)-6,6'-dichloro - 9 - ethyl-benzthio-carbocyanine iodide and 1,1'-di-(β-carboxyethyl)-6,6'-dimethoxy - 9 - ethyl-benzthio-carbocyanine.

4. A process for the preparation of color photographic emulsions for the production of the magenta image which comprises forming a silver halide emulsion sensitized with a compound having the formula

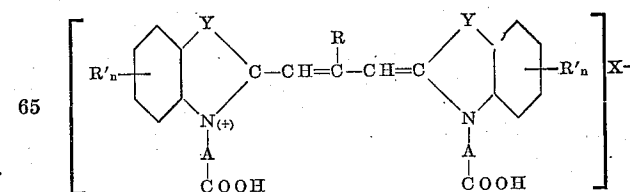


wherein one R₁ is a lower alkyl radical and the other R₁ is —A—COOH wherein A is a lower alkylene radical, R' is selected from the group consisting of hydrogen, lower alkyl, lower alkoxy, naphthylene and halogen, n is an integer from 1 to 2, Y is selected from the group consisting of selenium and sulfur atoms and X is an anion, forming in the absence of an oil former a dispersion of a pyrazolone color coupler lacking solubilizing groups and having an aliphatic hydrocarbon residue having 10 to 21 carbon atoms and mixing the said silver halide emulsion and the said dispersion to form the desired color photographic emulsions.

5. The process of claim 4 wherein the pyrazolone color coupler is selected from the group consisting of 1-phenyl-3-stearoylamino-pyrazolone-5, 1-(2',4'-dichlorophenyl)-3-heneicosyl-pyrazolone-5, 1-(2',4',6'-trichlorophenyl)-3-heptadecylamino-pyrazolone-5 and 1-phenyl-3-heptadecyl-pyrazolone-5.

6. The process of claim 4 wherein the sensitizer is selected from the group consisting of 1-(β-carboxyethyl)-1'-ethyl-6,6'-dimethoxy-benzeleno-pseudocyanine iodide, 1-(β-carboxyethyl)-1'-ethyl-5-methyl - 6,6' - dimethoxy-benzeleno-pseudocyanine iodide and 1-(β-carboxyethyl)-1'-ethyl-6-phenyl-6'-methoxy-benzthio-pseudocyanine.

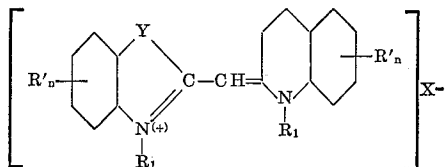
7. A process for the preparation of multi-layer photographic media capable of producing the cyan image and the magenta image which comprises coating a film support with a silver halide emulsion lacking solution promoters and containing as the sensitizer a compound selected from the group consisting of a compound having the formula



wherein R is a lower alkyl radical, R' is selected from the group consisting of hydrogen, lower alkyl radicals, lower alkoxy radicals, naphthylene and halogen, n is an integer from 1 to 2, A is a lower alkylene radical, Y is selected from the group consisting of selenium and sulfur atoms and X is an anion and its betaine derivatives and

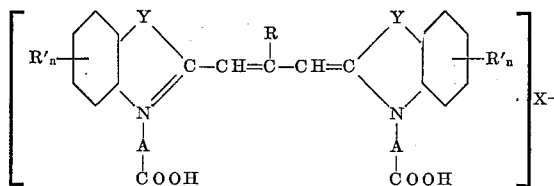
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a color coupler selected from the group consisting of phenols and α -naphthols lacking solubilizing groups and having an aliphatic hydrocarbon residue having 10 to 21 carbon atoms and superimposing thereon a silver halide emulsion lacking solution promoters and containing as the sensitizer a compound having the formula



wherein one R_1 is a lower alkyl radical and the other R_1 is $-\text{A}-\text{COOH}$ wherein A is a lower alkylene radical, R' is selected from the group consisting of hydrogen, lower alkyl, lower alkoxy, naphthylene and halogen, n is an integer from 1 to 2, Y is selected from the group consisting of selenium and sulfur atoms and X is an anion, and a pyrazolone color coupler lacking solubilizing groups and having an aliphatic hydrocarbon residue having 10 to 21 carbon atoms, then a yellow filter layer and finally an unsensitized emulsion layer containing a dispersed yellow coupler.

8. A color photographic emulsion for the production of the cyan image lacking solution promoters comprising a silver halide emulsion containing as the sensitizer a compound selected from the group consisting of a compound having the formula

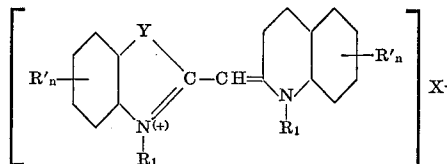


wherein R is a lower alkyl radical, R' is selected from

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the group consisting of hydrogen, lower alkyl radicals, lower alkoxy radicals, naphthylene and halogen, n is an integer from 1 to 2, A is a lower alkylene radical, Y is selected from the group consisting of selenium and sulfur atoms and X is an anion and its betaine derivatives and a color coupler selected from the group consisting of phenols and α -naphthols lacking solubilizing groups and having an aliphatic hydrocarbon residue having 10 to 21 carbon atoms.

9. A color photographic emulsion for the production of the magenta image lacking solution promoters comprising a silver halide emulsion containing as the sensitizer a compound having the formula



wherein one R_1 is a lower alkyl radical and the other R_1 is $-\text{A}-\text{COOH}$ wherein A is a lower alkylene radical, R' is selected from the group consisting of hydrogen, lower alkyl, lower alkoxy, naphthylene, and halogen, n is an integer from 1 to 2, Y is selected from the group consisting of selenium and sulfur atoms and X is an anion and a pyrazolone color coupler lacking solubilizing groups and having an aliphatic hydrocarbon residue having 10 to 21 carbon atoms.

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