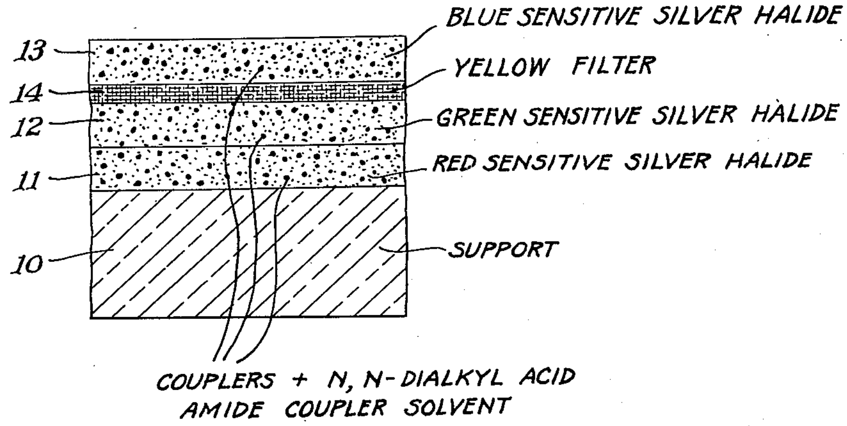
Dec. 12, 1950 G. W. SAWDEY ET AL 2,533,514

PHOTOGRAPHIC EMULSIONS CONTAINING COLOR COUPLERS AND AMIDE COUPLER SOLVENTS

Filed Nov. 19, 1947



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Patented Dec. 12, 1950 2,533,514

UNITED STATES PATENT OFFICE

2,533,514

PHOTOGRAPHIC EMULSIONS CONTAINING COLOR COUPLERS AND AMIDE COUPLER SOLVENTS

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Application November 19, 1947, Serial No. 787,016

10 Claims. (Cl. 95—7)

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This invention relates to color photography and particularly to novel coupler solvents for color-formers used in color-forming development in color photography.

The incorporation in silver halide emulsion layers of compounds which are capable of combining with the oxidation product of developing agents to produce dye images has been proposed many times. In 1913 Rudolf Fischer suggested a process of three-color photography which involved the incorporation of couplers or color-forming compounds in three differentially color-sensitized emulsion layers, each coupler capable of producing a color complementary to the sensitivity of the layer in which it was incorporated (Fischer U. S. Patent 1,055,155, March 4, 1913). The couplers suggested were compounds containing phenolic hydroxyl or active methylene groups which were capable of reacting with the development product of aromatic amino developing agents on photographic development to form dyes of the indophenol, indoaniline and azomethine classes.

A still different method of incorporating couplers in emulsion layers has been proposed in Martinez U. S. Patent 2,269,158, granted January 6, 1942, and in Mannes and Godowsky U. S. Patents 2,304,939 and 2,304,940, both granted December 15, 1942. According to the methods of these patents, the coupler is mixed with a water-insoluble colloid such as a natural or synthetic resin or a cellulose ester and the mixture of the coupler and the water-insoluble colloid is dispersed in a gelatin emulsion. One of the advantages of these methods is that it is frequently unnecessary to increase the molecular weight of the coupler appreciably in order to prevent diffusion of the coupler in the emulsion. The existence of an interface between the materials in which the coupler is incorporated, that is, the water-insoluble cellulose esters or resins, and the gelatin of the emulsion, prevents wandering of the coupler. A further advantage of this method is that the couplers may be incorporated in their neutral form, that is, it is not necessary to form the sodium salt of the coupler as in the case of previous methods. The colloidal materials with which the couplers are mixed in these processes are usually solids at room temperature and, in order to incorporate the mixture in an emulsion, it is necessary to dissolve it in a volatile solvent for both the coupler and the colloidal material and to incorporate the solution in the emulsion after which the volatile solvent is removed, either in a separate step or in the natural process of drying the coated emulsion layer.

In processes of the latter type, difficulties arise in some cases due to the solid nature of the final

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particles in which the couplers are incorporated. One of these difficulties is due to the limited solvent action which the solid colloid material has for the coupler and the dye derived from it, which increases the tendency for the coupler or dye, or both, to separate as a crystalline deposit on aging of the finished emulsion coatings. Furthermore, it is in some cases difficult to find a colloid material having the necessary solvent action for the coupler which is also sufficiently permeable to the processing solutions.

An improved method of incorporating couplers in emulsion layers consists in dispersing the couplers in a water-insoluble crystalloidal material, such as tricresyl phosphate, which have high solvent action for the coupler compound and a dye subsequently formed from it. This process is described in the Jelley and Vittum U. S. Patent 2,322,027, granted June 15, 1943.

We have discovered a class of compounds having superior solvent properties for couplers and dye images which result in emulsion layers capable of producing improved definition and resolving power.

It is, therefore, one object of the present invention to provide novel coupler solvents having improved solvent properties. Another object is to provide emulsion layers giving better definition and resolving power. Other objects will appear from the following description of our invention:

These objects are accomplished by emulsifying or dispersing couplers in photographic emulsion layers by means of the novel coupler solvents.

In the accompanying drawings is shown an enlarged cross-sectional view of a color film, the emulsions of which are made by using the coupler solvents of our invention.

The novel coupler solvents of our invention are, for example, the following:

N,N-diethyllauramide
N,N-di-n-butyllauramide
N,N-diethylstearamide
N,N-di-n-butylstearamide
N,N-diethylcapramide
N,N'-tetraethylsebacamide
N,N-dipropyl acetamide
N,N-ethyl butyl lauramide
N,N-didecyl lauramide
N,N-dinonyl stearamide
N,N-dibutyl arachidamide
N,N-dibutyl caproamide
N,N'-tetrabutyl succinamide
N,N'-tetrahexyl adipamide
N,N'-tetradecyl malonamide

In all of the above compounds the N-alkyl groups are the "normal" straight chain alkyl substituents; however, we contemplate as a part of our invention those alkyl substituents having branched chains totaling up to ten carbon atoms and falling within the formula given hereinafter.

The above compounds are classifiable as compounds having the formula:

$$R{-}CO{-}N\begin{matrix}\diagup R_1\\ \diagdown R_2\end{matrix}$$

where R is either an alkyl group of from 1 to 19 carbon atoms, or the group:

$$\begin{matrix}R_3\diagdown\\ R_4\diagup\end{matrix}N{-}CO{-}(CH_2)_n{-}$$

in which R_1, R_2, R_3 and R_4 are alkyl groups of from 2 to 10 carbon atoms and n is an integer from 1 to 12. In the above formula the groups R_1, R_2, R_3 and R_4 can be the same or different alkyl groups, so as to constitute symmetrical or unsymmetrical compounds. One prerequisite of the compounds useful in our invention is that they be liquid or form with the coupler compound a liquid system at ordinary temperatures. Otherwise the compounds will crystallize in emulsion layers which is, of course, not desirable. Furthermore, compounds having the above structure must have sufficiently high boiling point (above about 175° C. at atmospheric pressure) that they will not evaporate from a photographic emulsion layer; e. g. dimethyl acetamide has too low a boiling point to be of much use in our invention.

The alkyl amides preferred for use in our invention are those made from sebacic, lauric and stearic acids, on the one hand, because they have the combination of properties of good solvent power for couplers and dyes and they are relatively cheap and available. Also, since the color of the dye image obtained in color-forming development depends not only on the type of coupler and developer compounds in use, but also the solvent used, the preferred compounds, together with the couplers and developing agents of general use, produce dyes having the most desirable light-absorption characteristics when used for color photography.

The novel coupler solvents are used in emulsion layers in amounts of the order of from 0.5 to 3.0 parts per part of coupler. The quantity selected is determined by the solvent power and the effect which the particular coupler solvent produces on the dye-absorption characteristics. It has been ascertained, and this is a distinct advantage of our coupler solvents, that when the coupler solvents previously known are used, four to six times as much is required to dissolve and disperse the same quantity of a given coupler in an emulsion. In other words, the high solvent power of the novel solvents permits use of smaller quantities of coupler solvents and as a consequence we can obtain thinner emulsion layers having the same amount of coupler per unit area. This in turn results in improved definition and resolving power. The coupler solvents further possess good permeability to color developers and other processing solutions and do not have deleterious effects on the color of dye images and stability of emulsion layers. Also, the novel solvents do not have a deleterious effect upon residual coupler left in an emulsion layer after processing.

According to the present invention there is provided a sensitive photographic silver salt emulsion, such as silver halide, having a water-soluble or permeable binder, such as gelatin, in which are dispersed discrete particles of coupler and high-boiling water-insoluble coupler solvent material, the nature and proportions of the coupler and the coupler solvent being so chosen that the particles are liquid under the conditions of coating and processing the emulsion. The invention, therefore, includes a sensitive photographic silver halide emulsion having a water-soluble or permeable binder such as gelatin in which are dispersed particles of oil-like consistency composed of coupler and high-boiling coupler solvent. In carrying out the invention, the coupler which has been mixed with the high-boiling organic compound to produce an oil-like mixture may be dispersed in water or gelatin solution or in any aqueous binder of colloidal character which is miscible with the silver halide emulsion. The dispersion may be effected with the aid of homogenizer, colloid mill or the like and the dispersions may be stabilized by the addition of emulsifying agents such as those of the well-known higher fatty alcohol sulfate type. The dispersion may also be formed by dispersing a solution of coupler, and crystalloidal material, in a solvent of low boiling point such as butyl acetate, with water or gelatin solution and subsequently removing the low-boiling solvent by evaporation. Here, also, an emulsifying agent may be used.

In our process it is important that the mixture of coupler and crystalloidal material be a liquid at ordinary temperatures. This forms liquid particles when the mixture of coupler and crystalloidal material is emulsified in water and mixed with a gelatin emulsion, these particles retaining the coupler in solution, yet being readily penetrated by the photographic developing solution and other processing baths.

In our process we prefer to use the customary gelatino-silver halide emulsions although other water-soluble colloidal materials can be used for the photographic emulsion such as agar or water-soluble synthetic resins. The emulsions may be used in single layer or in multi-layer coatings and our invention is especially designed for the production of multi-layer coatings for natural color photography.

The drawing shows a multi-layer color film composed of differentially light-sensitive silver halide emulsion layers **11**, **12** and **13** carried by the support **10** of a cellulose ester or the like, layers **11**, **12** and **13** containing blue, green and red sensitive silver halide, respectively, and globules of a mixture of a coupler and an acid amide coupler solvent. As is usual, the coupler in the blue-sensitive layer **13** can be one forming yellow dye, that in layer **12** forming magenta dye and that in layer **11** forming cyan dye. The yellow filter layer **14** of dye or colloidal silver separates layers **12** and **13** and allows selective exposure of layers **11**, **12** and **13**. As is apparent, one or more of layers **11**, **12** and **13** can contain one of the novel coupler solvents, the other layers, for example, containing one of the coupler solvents of the Jelley et al. patent mentioned, or mixtures of the novel solvents with other coupler solvents can be used.

The coupler solvents of our invention have the "oil former" properties as described in U. S. Patent 2,322,027, that is, they produce an oily or liquid solution when mixed with the coupler, even though the coupler is a solid.

It is sometimes advantageous to employ a mixture of two or more of the novel coupler solvents in the same dispersion in order to obtain the desired combination of properties. Thus, one might use a mixture of one compound having exceptionally good solvent action, with another compound added in correct proportions to give the final dispersion the desired refractive index or to impart the desired absorption characteristics to the dye image.

The following example which is illustrative only shows the method of incorporating a coupler in an emulsion layer by means of the novel coupler solvents.

Example.—One gram of the coupler (2-(2',4'-di-tertiary amylphenoxyacetamino) - 4,6-dichloro-5-methylphenol) is dissolved in 0.5 cc. of N,N-di-n-butyl-lauramide by heating at 120° C. The warm solution is poured into a mixture of 18 cc. of 10% gelatin, 2 cc. of water, 2 cc. of a 10% solution of sodium tri-isopropylnaphthalene sulfonate. The mixture is then emulsified by passing through a colloid mill, and is then ready for mixing with the sensitive silver halide emulsion for coating. After coating the emulsion on a suitable support and drying it in the usual manner, development with 2-amino-5-diethylaminotoluene as developing agent and subsequently removing the silver image, a cyan dye image is obtained. In general, we dissolve the coupler in the coupler solvent by heating as above, but, if desired, we may, in addition, employ a small amount of a solvent such as alcohol or an organic acid ester to hasten solution. Otherwise, the novel coupler solvents are incorporated in the emulsions in the manner of the above example. Other wetting agents in the same or different quantities besides that shown in the above example may be used. Also, the amount and type of colloid vehicle can be varied and need not be gelatin but can be composed of a resin such as polyvinyl alcohol or a partially hydrolyzed polyvinyl ester, partially hydrolyzed cellulose esters and the like, in which sensitive silver salts such as silver halide can be dispersed.

The following couplers are given as illustrative of the wide number of couplers containing phenolic hydroxyl or the active methylene groups which are useful in conjunction with the novel coupler solvents:

β-(p-tert. butylphenoxy) ethyl-p-(ω - benzoylacetamino) -benzene sulfonate

2 - chloro - 5 - [N - (p-isopropyl benzyl) -N-(p-sec. amyl benzoyl) -amino] -1-naphthol

1-phenyl-3-pentadecyl-5-pyrazolone

1-(p - tert. butylphenoxyphenyl) -3-[m-(p-tert. amyl phenoxy) benzoyl-amino] -5-pyrazoline.

1-phenyl - 3 - palmityl amino - 4 - (p-methoxyphenylazo) -5-pyrazolone

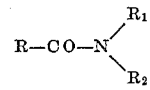
Other couplers which may be used are those such as disclosed in Weissberger U. S. Patent 2,350,138, granted May 30, 1944; Porter et al. U. S. Patent 2,369,489, granted February 13, 1945; Kodak British Patent 536,939, accepted June 3, 1941, and the colored couplers such as disclosed in Glass et al. U. S. Patent applications 533,930 and 533,932, both filed May 3, 1944, now U. S. Patents 2,453,661, granted November 9, 1948, and 2,455,169, granted November 30, 1948.

The novel coupler solvents of our invention are prepared in a well-known manner by reaction of an acid chloride with an amine corresponding respectively to the particular coupler solvents in the above-mentioned list.

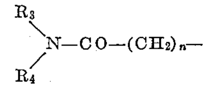
The invention having been described, we would have it understood that the disclosure herein is by way of example, and included in the invention are all modifications and equivalents falling within the scope of the appended claims.

What we claim is:

1. A light-sensitive photographic emulsion for producing a colored image comprising finely-divided liquid particles of a mixture of a color former compound capable of reacting with the oxidation product of a primary aromatic amino developing agent and a compound of boiling point above about 175° C., having the structure

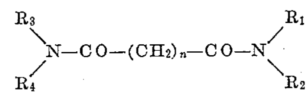


where R is a member of the group consisting of alkyl groups of from 1 to 19 carbon atoms, and the group



in which R_1, R_2, R_3, and R_4 are alkyl groups of from 2 to 10 carbon atoms and n is an integer from 1 to 12, said particles being dispersed in a light-sensitive silver halide-organic colloid emulsion.

2. A light-sensitive photographic emulsion for producing a colored image comprising finely-divided liquid particles of a mixture of a color former compound capable of reacting with the oxidation product of a primary aromatic amino developing agent and a compound of boiling point above about 175° C., having the structure

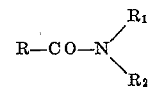


where R_1, R_2, R_3 and R_4 are alkyl groups of from 2 to 10 carbon atoms and n is an integer from 1 to 12, said particles being dispersed in a light-sensitive silver halide-organic colloid emulsion.

3. A light-sensitive photographic emulsion compounded according to claim 2 wherein the integer of the coupler solvent formula is 8.

4. A light-sensitive photographic emulsion for producing a colored image comprising finely-divided liquid particles of a mixture of a color former compound capable of reacting with the oxidation product of a primary aromatic amino developing agent and N,N'-tetraethyl sebacamide, said particles being dispersed in a light-sensitive silver halide-organic colloid emulsion.

5. A light-sensitive photographic emulsion for producing a colored image comprising finely-divided liquid particles of a mixture of a color former compound capable of reacting with the oxidation product of a primary aromatic amino developing agent and a compound of boiling point above about 175° C., having the structure



where R is an alkyl group of from 1 to 19 carbon atoms, and R_1 and R_2 are alkyl groups of from 2 to 10 carbon atoms, said particles being dispersed in a light-sensitive silver halide-organic colloid emulsion.

6. A light-sensitive photographic emulsion for producing a colored image comprising finely-divided liquid particles of a mixture of a color former compound capable of reacting with the oxidation product of a primary aromatic amino

developing agent and a compound of boiling point above about 175° C., having the structure

$$C_{11}H_{23}-CO-N\begin{matrix}\diagup R_1\\ \diagdown R_2\end{matrix}$$

where R_1 and R_2 are alkyl groups of from 2 to 10 carbon atoms, said particles being dispersed in a light-sensitive silver halide-organic colloid emulsion.

7. A light-sensitive photographic emulsion for producing a colored image comprising finely-divided liquid particles of a mixture of a color former compound capable of reacting with the oxidation product of a primary aromatic amino developing agent and N,N-dibutyl lauramide, said particles being dispersed in a light-sensitive silver halide-organic colloid emulsion.

8. A light-sensitive photographic emulsion for producing a colored image comprising finely-divided liquid particles of a mixture of a color former compound capable of reacting with the oxidation product of a primary aromatic amino developing agent and a compound of boiling point above about 175° C., having the structure

$$C_{17}H_{35}-N\begin{matrix}\diagup R_1\\ \diagdown R_2\end{matrix}$$

where R_1 and R_2 are alkyl groups of from 2 to 10 carbon atoms, said particles being dispersed in a light-sensitive silver halide-organic colloid emulsion.

9. A light-sensitive photographic emulsion for producing a colored image comprising finely-divided liquid particles of a mixture of a color former compound capable of reacting with the oxidation product of a primary aromatic amino developing agent and N,N-diethyl stearamide, said particles being dispersed in a light-sensitive silver salt emulsion.

10. A multi-layer photographic element comprising at least one light-sensitive silver halide-organic colloid emulsion layer containing finely-divided liquid particles of a mixture of a color former compound capable of reacting with the oxidation product of a primary amino developing agent and a compound of boiling point above about 175° C., having the structure

$$R-CO-N\begin{matrix}\diagup R_1\\ \diagdown R_2\end{matrix}$$

where R is a member of the group consisting of alkyl groups of from 1 to 19 carbon atoms, and the group

$$\begin{matrix}R_3\diagdown\\ R_4\diagup\end{matrix}N-CO-(CH_2)_n-$$

in which R_1, R_2, R_3, and R_4 are alkyl groups of from 2 to 10 carbon atoms and n is an integer from 1 to 12.

GEORGE W. SAWDEY.
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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,322,027	Jelley et al. ________	June 15, 1943

Certificate of Correction

Patent No. 2,533,514 December 12, 1950

GEORGE W. SAWDEY ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 8, line 4, strike out the word "salt" and insert instead *halide-organic colloid*; line 10, after "primary" insert *aromatic*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 3rd day of April, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.