

## UNITED STATES PATENT OFFICE

2,299,641

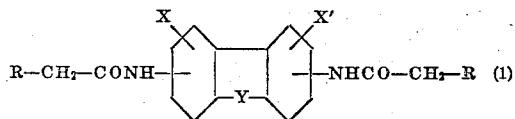
## PROCESSES OF COLOR PHOTOGRAPHY AND COMPOSITIONS AND ELEMENTS THEREFOR

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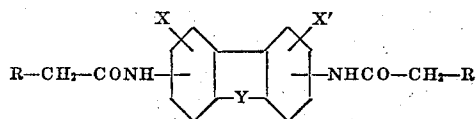
This invention relates to color photography. More particularly it relates to photographic elements, emulsions and developer solutions containing symmetrical di-acyl-acet-amino derivatives of trinuclear organic ring compounds. Still more particularly it relates to photographic elements bearing at least one emulsion layer which contains as a color-former a symmetrical compound of the general formula:



in which R represents an acyl group, X and X' are the same or different and represent hydrogen or substituent groups including one or more water-insolubilizing groups or solubilizing groups, and Y represents a bivalent radical. The invention also relates to processes of producing photographic images in the presence of such compounds.

This invention has for an object the production and use of photographic emulsions and developer solutions containing novel color-formers. A further object is the preparation of photographic emulsion layers containing novel color formers of the above type which are immobile and form colored images of good strength, stability and color for color photography. A still other object is to form color-former compositions which couple readily upon development of silver images to form water-insoluble immobile dyes. Still other objects will be apparent from the following disclosure.

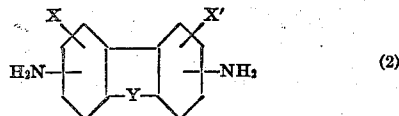
The above objects are attained by the following invention which involves the preparation and use of developer solutions and especially photographic emulsions containing a symmetrical di-acylacetamino derivative of a trinuclear organic ring compound of the general formula:



in which R represents an acyl group, X and X' are the same or different and represent hydrogen or substituent groups including one or more water-insolubilizing groups or water solubilizing groups, and Y represents a bivalent radical. The term "bivalent bridge radical" as used herein is defined to mean  $-CH_2-$ ,  $-CO-$ ,  $-CH=CH-$ ,  $-CH_2CH_2-$ ,  $-NH-$ ,  $-N\text{-alkyl-}$ ,  $-O-$ ,  $-S-$ ,  $-N=N-$ ,  $-N=NO-$ ,  $-SO_2-$ , and  $-COCO-$ .

The term "acyl" as used herein is defined to mean the acyl radical  $RCO-$  corresponding to a carboxylic acid. The group  $RCO-$  may be derived from various aliphatic, isocyclic and heterocyclic acids. Representative radicals falling within this class include propionyl-, butyryl-, decanoyl-, benzoyl-, 4-chlorobenzoyl-, 4-nitrobenzoyl-, alpha-naphthoyl-, furoyl- and thi-enoyl-, N-heterocyclic carboxylic acyl radicals, e. g. picolinoyl, nicotinoyl, isonicotinoyl, etc.

The novel color formers hereof may be prepared by reacting a diamine of the general formula:



wherein the symbols have the same meaning as set forth in Formula 1, with an acyl-acetylating agent, preferably an ester of an acyl-acetic acid. The condensation may be carried out in the presence of a solvent or diluent such as chloro-benzene, xylene, nitro-benzene, etc. The proportions of the reactants may be varied but in general they should be used in the ratio of about one mol of the diamino compounds to at least two mols of the acyl acylating agent.

The above-described compounds are not a part of the present invention which is concerned with their photographic uses as color formers. They may be incorporated in developer solutions in various known manners, for example, by dissolving them in an organic solvent miscible with water and adding the solution to the aqueous developer solution. They may, if their solubility is sufficient, be added directly to the bath. In some cases, the use of dispersing agents such as alkylated naphthalene sulfonates, higher aliphatic alcohol sulfates, higher alkyl sulfonates, mineral oil sulfonates, Turkey red oil, etc., may be employed.

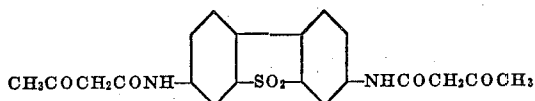
The color formers may be incorporated into emulsions in the conventional manners by dissolving them in a solvent which does not affect the sensitivity of the emulsion and intimately mixing the same with the gelation solution or emulsion. A small amount of an alkali metal base is sometimes advantageous in obtaining a rapid and uniform dispersion of the color-former throughout the emulsion. Various emulsion components may be present without affecting dye formation. The compounds are remarkably free of deleterious effects on the photographic sensi-

tivity and chromatic response characteristics of silver halide emulsions, e. g. silver chloride, silver bromide, and silver chloro-bromide, silver-bromo-iodide, etc. emulsions. They may likewise be used in conjunction with the known sensitizing dyes which render the emulsions sensitive to certain additional wave-length regions of light. They may also be used in conjunction with emulsion desensitizers, surface modifiers and emulsion hardening agents.

The invention will be further illustrated but is not intended to be limited by the following examples:

#### Example I

To 100 cc. of 2% by weight aqueous gelatin solution is added a solution consisting of 8 cc. of ethyl alcohol containing NaOH and 1 gram of the compound having the formula:



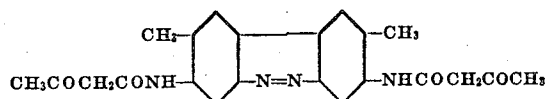
prepared by reacting 4,4'-diaminodiphenyl-2,2'-sulfone with ethyl-acetoacetate. The total weight of the combined solution is then brought to about 150 grams with water and then the mixture is added to 100 grams of a gelatino-silver halide emulsion and mixed thoroughly. The resulting emulsion may then be coated upon a suit-

able support such as paper, glass or a cellulose derivative base, or upon another photographic emulsion layer which may or may not be another color-forming dye component. After exposure directly in a camera or by printing through appropriate color records, the film is developed in a non-color-forming developer. The reversed image is then developed by means of an alkaline solution of diethyl-p-phenylenediamine, whereupon a light yellow of good strength and color forms in situ with metallic silver.

In place of the diaceto-acetyl benzidine sulfone may be substituted diaceto-acetyl tolidine sulfone which produces a yellow dyed image. Similarly, diacetoacetyl-5,5'-dichlorobenzidine sulfone, 4,4'-di-(benzoyl-acetyl-amino)-5,5'-dimethyldiphenyl-2,2'-sulfone, 4,4'-di-(para-nitrobenzoyl-acetyl-amino)-5,5'-dimethyldiphenyl-2,2'-sulfone, 4,4'-di-(alpha-furoyl-acetyl-amino)-5,5'-dimethyl-diphenyl-2,2'-sulfone, difuroylacetyl-tolidine sulfone, dipicolinoyl acetyl-tolidine sulfone and dibenzylacetyl-tolidine sulfone may be substituted which result in yellow colored dye images.

#### Example II

To 100 cc. of 2% by weight aqueous gelatin solution is added a solution consisting of 8 cc. of ethyl alcohol containing NaOH and 1 gram of the compound having the formula:

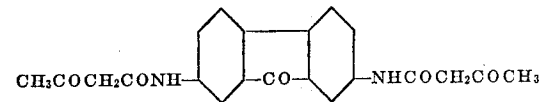


prepared by reacting tolidine azone with ethyl acetoacetate. The total weight of the combined solution is then brought to about 150 grams with water and then the mixture is added to 100 grams of a gelatino-silver halide emulsion and mixed

thoroughly. The resulting emulsion may then be coated upon a suitable photographic support after the manner described in Example I. After exposure, the photographic element is developed in an alkaline solution containing diethyl-p-phenylene diamine whereupon a yellow dye of good tinctorial strength is formed. In place of the tolidine azone of this example may be substituted the related tolidine azone mono-oxide which contains the bridge radical  $-\text{N}=\text{NO}-$ .

#### Example III

To 100 cc. of 2% by weight aqueous gelatin solution is added a solution consisting of 8 cc. of ethyl alcohol containing NaOH and 1.5 grams of the compound having the formula:

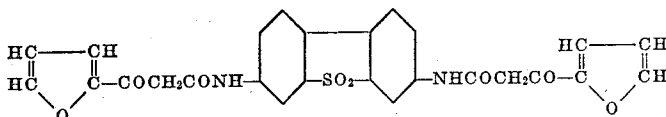


prepared from 4,4'-diamino-fluorenone and ethyl-acetoacetate.

Similar results were obtained with 4,4'-diacetyl-acetamino-phenanthraquinone.

#### Example IV

To 100 cc. of 2% by weight aqueous gelatin solution consisting of 8 cc. of ethyl alcohol containing NaOH and 1.5 grams of the compound having the formula:



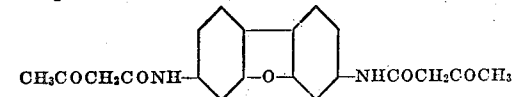
together with a 20% aqueous caustic soda solution in an amount equal to 2 mols of alkali for each mol of the compound. The total weight of the combined solution is then brought to about 150 grams with water and then the mixture is added to 100 grams of a gelatino-silver halide emulsion and mixed thoroughly. The resulting emulsion may then be coated upon a suitable photographic support after the manner described in Example I. After exposure the photographic element is developed in an alkaline solution containing dimethyl-p-phenylene diamine, whereupon a yellow dye light in color and of good tinctorial strength is formed.

#### Example V

To 100 cc. of a developer having the following composition:

|                                          |                   |      |
|------------------------------------------|-------------------|------|
| Diethyl-p-phenylenediamine hydrochloride | grams             | 2    |
| Sodium sulfite (anhydrous)               | do                | 5    |
| Sodium carbonate (anhydrous)             | do                | 20   |
| Water                                    | cubic centimeters | 1000 |

are added from 0.1 to 1.0 gram of the following compound:



prepared from 4,4'-diamino-diphenyl-2,2'-oxide and ethyl-acetoacetate dissolved in a few cc. of alcoholic sodium hydroxide. An exposed photographic element containing exposed silver salts is developed in aforedescribed solution to form a yellow dyed image. The silver was removed by Farmer's reducer.

Similar results are obtained with the corresponding sulfur analogue.

In place of the specific color formers set forth in the above examples may be substituted other compounds or mixtures of compounds which have the chemical structure set forth above. Thus, compounds similar to those of the specific examples, but containing as a bivalent bridge radical a  $-\text{CH}_2-$ ,  $-\text{CH}=\text{CH}-$ ,  $-\text{CH}_2-\text{CH}_2-$ ,  $-\text{NH}-$ ,  $-\text{N}-$ alkyl-group which may be prepared from the corresponding bases may be substituted.

The benzo nuclei of the trinuclear ring compounds may be substituted by one or more water insolubilizing or solubilizing groups as above stated. Water solubilizing groups, e. g. hydroxyl sulfonic and carboxylic are preferred, but water-insolubilizing groups, e. g. alkyl, alkoxy, halogen and nitro may be used. Suitable groups include methyl, ethyl, butyl, decyl, dodecyl, octadecyl, etc., methoxy, ethoxy, butoxy, decoxyl, octadecoxyl, etc.; chlorine, bromine, etc.

When R represents an aroyl or a heterocyclic acyl group it is to be further understood that this nucleus may be further substituted with water-insolubilizing groups or solubilizing groups of the same type which may be present in the benzo nuclei.

The amino groups of the trinuclear amines may occupy various positions on the benzo nuclei of such compounds. For instance, they may occupy the 6-6', 5-5', 4-4', as well as similar free positions. The 4-4' diamino derivatives are preferred.

The color formers described herein may be produced by the condensation of trinuclear diamines with esters of acyl-acetic acids. This condensation may be effected by the treatment of the diamines with an excess of the ester under proper conditions of time and temperature, such conditions being capable of considerable variation without appreciably affecting the results. Alternatively, the condensation may be carried out in a solvent or diluent such as chloro-benzene, xylene, nitrobenzene, etc., using approximately equivalent quantities of the diamino compound and ester.

Some of the color formers may likewise be prepared by the action of the dimer of ketene (referred to both as acetyl-ketene and cyclobut-1:3-dione). Here again the reaction may be carried out by heating the diamine with an excess of the acyl-acetylating agent or by dissolving or suspending it in an inert solvent and treating it with approximately an equivalent quantity of the ketene-dimer. This method of preparation is, of course, applicable only to the production of those products in which the acyl residue is an acetyl group.

The dye intermediates used in this invention are not limited in their utility to any one process of color photography. They are suitable for dye coupling development with arylene-diamino developing agents, and by suitably controlling the molecular weights of the products, they may be used in the color developer or in the photographic emulsion. Furthermore, the dye components of this invention couple with diazo compounds, so that they are therefore suitable for transforming into azo dyes, followed or not by differential bleaching in the presence of silver images as is known in the art.

The development process used in carrying out this invention may be applied either to a latent image in an emulsion of a silver halide which has been exposed to light and which may or may not contain the novel color formers hereof. The

exposures having been made in a camera or by printing through a photographic negative image. Or it may be applied to the residual unaltered silver salt left where an initial reduced silver image has been dissolved away as in a reversal process of development. Or it may be applied to a developed photographic image in metallic silver which has been fixed by the removal of unaltered silver halides by means of solvents and subsequently converted to a developable silver salt by means of known photographic bleaching agents.

For instance, a silver halide emulsion layer containing one of the herein described color-formers which has been exposed and developed to a silver image and fixed, is treated with a diazo or tetrazo salt and converted into a colored image by the process of Christensen, (U. S. 1,517,049).

The preferred developing agents in the process of dye coupling development are derivatives of p-phenylenediamine and particularly the asymmetric dialkyl p-phenylenediamines, e. g., p-aminodimethylaniline, p-aminodiethylaniline, p-aminodibutylaniline, etc. Other developing agents which may be used include p-phenylene diamine itself, p-methylaminoaniline, p-ethylaminoaniline, p-aminophenol, N,N-diethyl-o-phenylenediamine, chloro-p-phenylenediamine, 1,2,5-toluylenediamine, 2-amino-5-diethylaminotoluene, N-p-aminophenylpiperidine, N-methyl-N-hydroxyethyl-p-phenylene diamine, N-butyl-N-hydroxy-ethyl-p-phenylenediamine,  $\beta$ - $\gamma$ -dihydroxypropyl-p-phenylenediamine, 2-amino-5-(N- $\beta$ -hydroxy-ethyl-N-butyl) aminotoluene and its dihydrochloride, 4-aminodiphenylamine, 2:4-diaminophenylamine, 4-amino-4'-hydroxy diphenylamine, etc. These aromatic amino-developing agents may be used in the form of their salts, which may be either inorganic or organic. The salts are, in general, more stable and soluble than the free bases. As examples of suitable salts mention is made of the hydrochloride, sulfates, acetates, etc.

Among the further advantages of the present invention is the fact that the compounds can be readily dispersed, especially those containing solubilizing groups, yet they are, surprising to say, non-migratory in the sense as applied to emulsion color-formers.

The compounds are clear and transparent in the emulsion areas which have not undergone developing coupling. The dyes obtained are of unusual brilliance, color saturation and fastness to light.

This application is a continuation-in-part of our copending application, Serial No. 215,702, filed June 24, 1938; now Patent Number 2,184,303, December 26, 1939.

As many apparently widely different embodiments may be made hereof without departing from the spirit and scope, it is to be understood that this invention is not to be limited to the specific embodiments herein except as defined by the appended claims.

We claim:

1. The process which comprises developing a photographic image with a dye coupling aromatic amino developing agent containing an unsubstituted amino group in the presence of a compound of the general formula:



