

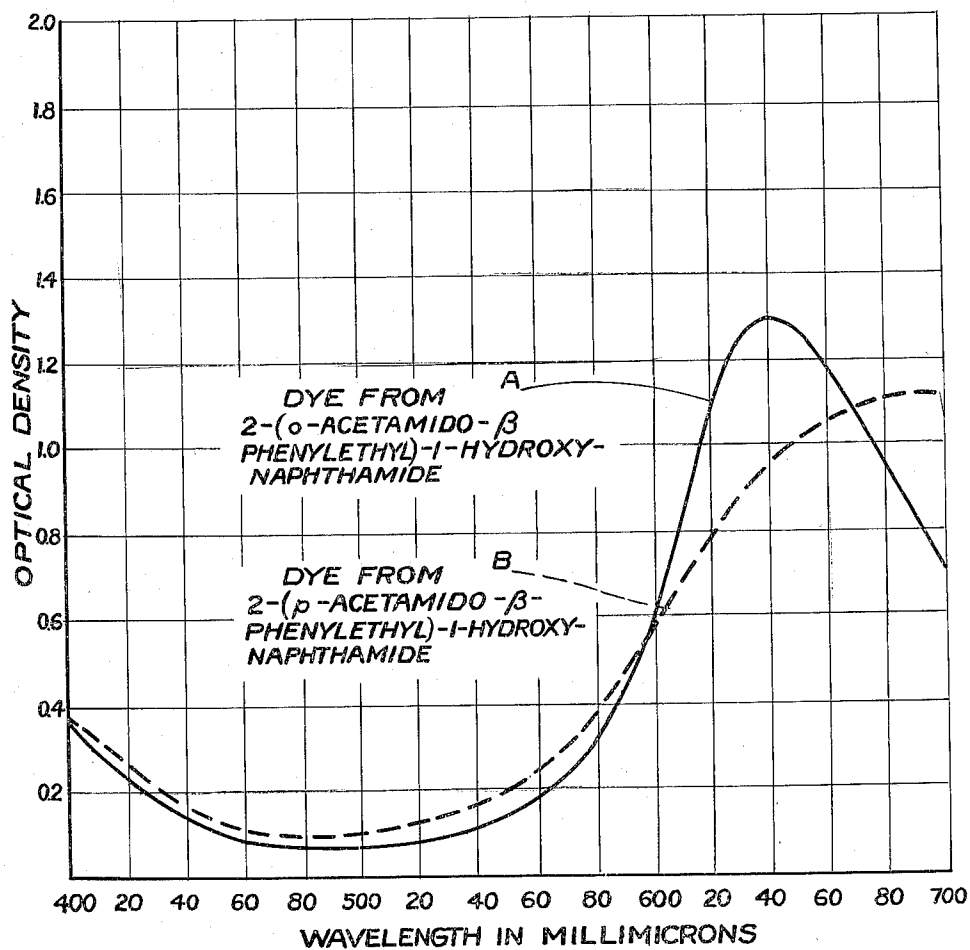
Oct. 3, 1961

P. W. VITTUM ET AL

3,002,836

CYAN COLOR FORMER FOR COLOR PHOTOGRAPHY

Filed April 9, 1959



Paul W. Vittum
Arnold Weissberger
INVENTORS

BY *R. Frank Smith*
L. H. Willis
ATTORNEYS

1

3,002,836 CYAN COLOR FORMER FOR COLOR PHOTOGRAPHY

Paul W. Vittum and Arnold Weissberger, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

Filed Apr. 9, 1959, Ser. No. 805,206

7 Claims. (Cl. 96-55)

This invention relates to color photography and to an improved coupler compound for use in developer compositions for developing colored photographic images.

The use of color-forming compounds which react with the oxidation products of primary aromatic amino developing agents to form color images upon photographic development is well known and has been the subject of numerous patents. The dyes formed in this way frequently are insoluble in water and in the ordinary photographic developing and fixing baths, although the silver images formed simultaneously with them during the photographic development may be removed from the photographic emulsion layer to leave pure dye images in the layer. The coupler compounds used in this way may be added to the developing solution and in certain cases can be incorporated in the photographic layer prior to exposure.

These color-forming compounds are ordinarily used in the subtractive process of color formation and the image dyes formed from them, that is cyan, magenta, and yellow, are intended to be complementary to the primary colors. The couplers used to produce the cyan dyes are usually phenols or naphthols and produce indaniline or indophenol dyes upon coupling with the oxidation products of the developing agent depending upon the particular developing agent used.

In order to be useful for color photography the dyes produced upon color development must have certain desirable light transmission or spectrophotometric characteristics. Thus, ideally the cyan or blue-green dye should absorb red light completely and transmit blue and green light completely. It should retain these transmission characteristics over a long period of time and should withstand reasonable exposure to heat and light without appreciable fading or loss of these light transmission characteristics. The other dyes should also exhibit selective absorption and transmission characteristics.

Many of the available cyan couplers, however, have been found not to produce dyes having these characteristics to the desired degree. Many of the naphthol and substituted naphthol couplers used as cyan color formers in color photography have higher green light absorption than is desired. Some of them have not had as high absorption of red light as desired.

It is, therefore, an object of the present invention to provide a photographic coupler compound for producing cyan dye images. A further object is to provide a coupler compound which produces a cyan dye having low green light absorption, but high red light absorption. A still further object is to provide a coupler compound which produces a dye having a high degree of heat and light stability. Other objects will appear from the following description of our invention.

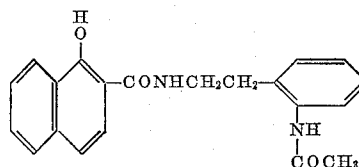
These objects are accomplished according to our invention by the use of 2-(o-acetamido- β -phenylethyl)-1-

2

hydroxy naphthamide as a coupler compound. This coupler forms dyes which are very valuable in color photography because of their low green and high red absorption characteristics. These properties of the dyes from our coupler are very unexpected because they are so much superior to those of the dyes formed from the coupler compound 2-(p-acetamido- β -phenylethyl)-1-hydroxy naphthamide which has been described as coupler 10 of Weissberger and Eden's U.S. Patent 2,589,004 granted March 11, 1952. Not only do the dyes from our coupler give very desirable spectrophotometric characteristics but they have good stability upon exposure to heat and light. Furthermore, the coupler is readily soluble in the developer solutions in which it is used and shows good reactivity with the oxidized developing agents.

The accompanying drawing shows spectrophotometric curves which compare the spectral absorptions of the dye images produced by the coupling reaction of our coupler with oxidized 2-amino-5-diethyl amino toluene hydrochloride as shown by curve A with the corresponding curve B for the dye produced by the coupling reaction of the coupler 2-(p-acetamido- β -phenylethyl)-1-hydroxy naphthamide with the same developer.

Our coupler 2-(o-acetamido- β -phenylethyl)-1-hydroxy naphthamide which may be represented by the following formula



was prepared by the following reactions. N-phenethylacetamide was prepared by acetylating phenethylamine with acetic anhydride. The acetylating reaction mixture was held below 100° C. during the reaction. After the reaction was completed excess acetic anhydride was removed and the product distilled at 155 to 159°/1 mm. The N-phenethylacetamide was nitrated. The p-nitro derivative was separated from the mixture of o- and p-nitro compounds formed and the o-nitro derivative was reacted with hydrobromic acid to form 1-nitro-2-phenethylamine hydrogen bromide. This was reacted with sodium hydroxide to form 1-nitro-2-phenethylamine which was then reacted with phenyl-1-hydroxy-2-naphthoate to produce 1-hydroxy-(2-nitrophenylethyl)-2-naphthamide. This compound was then reduced to the corresponding amine by boiling under reflux in the presence of granular iron powder and acetic acid. The amine was then acetylated by reacting it with acetic anhydride to produce our coupler.

Another method used to prepare our coupler is given below. Ethyl-o-nitrophenylpyruvate was prepared by reacting diethyl oxalate with o-nitrotoluene. This compound was heated with water on a steam bath to produce o-nitrophenylpyruvic acid which was treated with hydroxylamine hydrochloride and the solution made basic with sodium hydroxide. After 3 hours, reaction time on a steam bath, the reaction mixture was cooled to room temperature and acidified with dilute sulfuric acid. This mixture was heated on a steam bath for 2 to 2½ hours after which the reaction mixture was cooled and the solid o-nitrophenylacetoneitrile was dried and crystallized from

3

n-propanol. This material, dissolved in ethyl alcohol, was reduced on a Parr shaker under a maximum of 55 p.s.i. of H_2 using palladium on carbon as catalyst. Following the hydrogenation the catalyst was filtered out and the product was crystallized by evaporation at reduced pressure on a water bath. 95% ethyl alcohol was used as a solvent in purifying the o-aminophenylacetonitrile by recrystallization. This material was acetylated with acetic anhydride in diethyl ether. The product o-acetamidophenylacetonitrile was reduced in alcohol and ammonia using a nickel catalyst at a maximum hydrogen pressure of 1800 p.s.i. at 100 to 105° C. After hydrogenation was completed the catalyst-free solution was evaporated on a steam bath at reduced pressure and the residue distilled at an oil pump vacuum. The liquid fraction o-acetamidophenylamine was condensed with phenyl-1-hydroxy-naphthoate. The purified product 1-hydroxy-N-(2-acetamidophenylethyl)-2-naphthamide had a melting point of 222 to 224° C.

The coupler was designed for use in processes in which the coupler is incorporated in the developing solution such as those described in Mannes and Godowsky U.S. Patent 2,113,329 granted April 5, 1938, or Mannes, Godowsky, and Wilder U.S. Patent 2,252,718 granted August 19, 1941.

The following composition illustrates a developer solution in which the coupler is used.

Example I

	G.
Sodium hydroxide.....	4.0
Sodium sulfite.....	10.0
2 - (o - acetamido - β - phenylethyl) - 1 - hydroxy naphthamide	1.5
2-amino-5-diethyl amino toluene hydrochloride....	2.5
Water to 1 liter.	

The developer composition may be varied from Example I depending upon the specific requirements that the color developer must satisfy. For example, it is possible to change the concentrations of the constituents in Example I. It is also possible to add other constituents to a developer such as shown in Example I. For example, any of the well-known antifoggants, silver halide solvents, competing couplers, competing developers and other constituents such as potassium bromide, potassium iodide, sodium carbonate, and sodium sulfate may be incorporated in developer compositions containing our coupler. Any color-forming developer containing a primary aromatic amino developing agent may be used. These include developers having two primary amino groups as well as those having one of the amino groups substituted or having substituents in the ring such as alkyl phenylenediamines and alkyl toluene diamines. These compounds are usually used in the salt form such as the hydrochloride or the sulfate which are more stable than the amines themselves. Suitable developing agents are diethyl-p-phenylenediamine hydrochloride, monomethyl-p-phenylenediamine hydrochloride, dimethyl-p-phenylenediamine hydrochloride and 2-amino-5-diethyl amino toluene hydrochloride. The p-aminophenols and their substitution products may also be used where the amino group is unsubstituted. All of these developers have unsubstituted amino groups which enable the oxidation products of the developer to couple with the color-forming compounds to form a dye image.

The preferred developer composition containing our coupler uses the developing agent 2-amino-5-diethyl amino toluene hydrochloride.

This developer composition is particularly valuable because of the unusual spectrophotometric characteristics of the cyan dye image it produces in light sensitive silver halide emulsion layers upon color development. It is thought that the unique spectrophotometric characteristics of the dye produced by this developer composition is due to the microcrystalline structure of the dye.

4

This microcrystalline structure of our dye is very unexpected since the corresponding dye produced by the coupler 2-(p-acetamido- β -phenylethyl)-1-hydroxy naphthamide and 2-amino-5-diethyl amino toluene hydrochloride, is amorphous in structure.

Another developer composition illustrating the use of our coupler in a preferred developer is given in the following example.

Example II

	G.
Sodium tetraphosphate.....	1.0
Sodium bromide.....	2.5
Potassium iodide.....	0.015
Sodium sulfite.....	10.0
Sodium sulfate.....	20.0
Sodium hydroxide.....	4.0
6-nitrobenzimidazole nitrate.....	0.15
Monobenzyl-p-amino phenol.....	0.5
2 - (o - acetamido - β - phenylethyl) - 1 - hydroxy naphthamide	1.5
2-amino-5-diethyl amino toluene HCl.....	2.5
Water to 1 liter.	
pH 12.5.	

Developers containing our coupler are used in color photographic processes for the formation of cyan colored images in light-sensitive silver halide emulsion layers. The light-sensitive silver halide emulsion layers may be those containing gelatin or other carrier such as collodion, organic esters of cellulose, or synthetic resins. The carrier may be supported by a transparent material such as glass, a cellulose ester, or a non-transparent medium such as paper or an opaque cellulose ester. The photographic light-sensitive emulsion may be coated as a single layer on the support or as superposed layers on one or both sides of the support. The superposed layers may be differently sensitized. Usually, the cyan-forming layer is used in conjunction with yellow and magenta image-forming layers for the purpose of natural color photography by the subtractive process. The superposed cyan, yellow and magenta image-forming layers may be arranged in any order on the support.

The following example illustrates a typical way in which our couplers are used in color developers for developing cyan dye images in exposed silver halide emulsion layers.

Example III

A film coated with an ordinary silver bromoiodide emulsion for color photography was exposed under an image at $\frac{1}{25}$ of a second with light having a color temperature of 3000° K. and developed for 10 minutes in a black-and-white developer having the composition:

	G.
2,4-diamino phenyl hydrochloride.....	5
Sodium sulfite.....	50
Potassium bromide.....	5
Water to 1 liter.	

The film was exposed through the base, then developed for 12 minutes in the color-forming developer described in Example II, washed, and then the silver image and the residual silver halide was removed by treating the film for 5 minutes in a conventional potassium ferricyanide-potassium bromide bleach, followed by fixing in a conventional hypo fixing bath for 5 minutes. After a 10-minute final wash the film was dried. The result was a positive dye image having λ_{max} value of 640 m μ .

The spectrophotometric curve for the cyan dye image produced in this film sample is depicted on the accompanying drawing as curve A. Spectrophotometric curve B of this drawing was made from a film sample of the same emulsion which was given the process of Example III, in which the color developer composition contained coupler 2-(p-acetamido- β -phenylethyl)-1-hydroxy naphthamide in place of the coupler of our invention.

The advantages of the dye from our coupler over the

prior art dye are readily apparent from a comparison of the light absorption characteristics shown by their respective spectrophotometric curves. Curve A shows that our dye has a lower absorption of light in the range of wave lengths from 400 through 595 m μ than does the corresponding prior art dye shown by curve B. This lowered absorption is particularly noticeable in the green to yellow region of the spectrum but extends up into the orange region. It will be noted that the absorption of our dye increases sharply from about 600 m μ and reaches a maximum at a wave length of 640 m μ . Not only is this a very valuable characteristic but the fact that our dye has a maximum absorption that is two-tenths of a density unit higher than the other dye makes our dye particularly desirable for color photography.

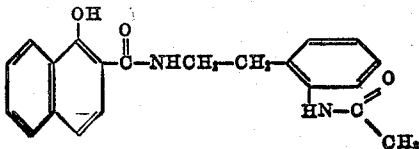
The unusual differences in the absorption characteristics between the dyes from the prior art coupler and our coupler are quite unexpected in view of the chemical similarity of the two compounds.

Our coupler is also valuable in color photography because it forms dyes having excellent stability upon exposure to heat and light. Furthermore, our coupler is readily soluble in the color developer solutions in which it is used and demonstrates good reactivity with oxidized developing agents during the development reactions.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A cyan-forming photographic developer comprising a phenylenediamine developing agent having at least one primary amino group and the coupler compound 2-(o-acetamido- β -phenylethyl)-1-hydroxynaphthamide having the formula:



2. In a method of preparing a cyan photographic image in an exposed silver halide emulsion layer, the step comprising developing said exposed silver halide emulsion layer in the presence of the coupler 2-(o-acetamido- β -phenylethyl)-1-hydroxynaphthamide in a color developer comprising a phenylenediamine developing agent having at least one primary amino group.

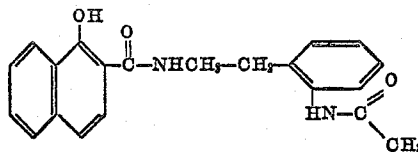
3. A cyan-forming photographic developer comprising the primary aromatic developing agent 2-amino-5-diethyl amino toluene hydrochloride and the coupler compound 2-(o-acetamido- β -phenylethyl)-1-hydroxy naphthamide.

4. A cyan-forming photographic developer comprising the primary aromatic amino developing agent N-ethyl- β -methanesulfonamidoethyl-3-methyl-4-amino aniline sulfate and the coupler compound 2-(o-acetamido- β -phenylethyl)-1-hydroxy naphthamide.

5. A cyan-forming photographic developer comprising the primary aromatic developing agent N-ethyl- β -methanesulfonamidoethyl-4-amino-aniline and the coupler compound 2-(o-acetamido- β -phenylethyl)-1-hydroxy naphthamide.

6. In a method of producing a cyan photographic image in an exposed silver halide emulsion layer, the step comprising developing said exposed silver halide emulsion layer in the presence of the coupler 2-(o-acetamido- β -phenylethyl)-1-hydroxynaphthamide in a color developer comprising the developing agent 2-amino-5-diethyl amino toluene hydrochloride.

7. The compound represented by the following formula:



References Cited in the file of this patent

UNITED STATES PATENTS

2,589,004 Weissberger et al. Mar. 11, 1952