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2-(O-PROPIONAMIDO-B-PHENYLETHYL)-1-HYDROXYNAPHTHAMIDE
AS A COLOR FORMER
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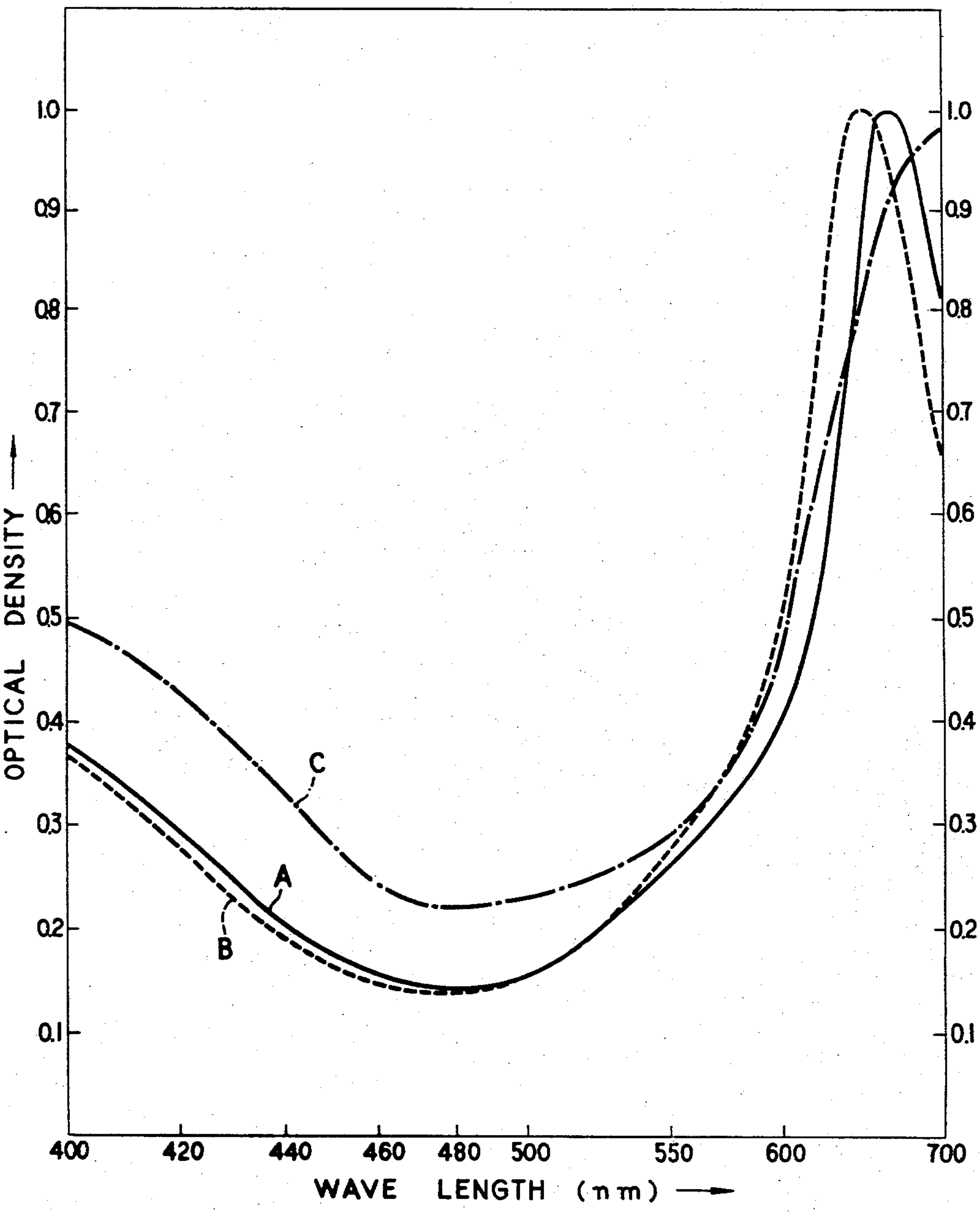

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PHOTOGRAPHIC DEVELOPER COMPOSITION CONTAINING 2-(o-PROPIONAMIDO-β-PHENYLETHYL) - 1 - HYDROXYNAPHTHAMIDE AS A COLOR FORMER

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1 Claim. (Cl. 96—55)

ABSTRACT OF THE DISCLOSURE

The novel color former 2-(o-propionamido-β-phenylethyl)-1-hydroxynaphthamide incorporated in a photographic developer composition containing 2-methyl-4-(N-ethyl-N-2-hydroxyethyl) aminoaniline sulfate reduces undesirable magenta dye formation in the cyan layer and of undesirable cyan dye in the other layers.

This invention relates to color photography and particularly to a color developer containing an improved color former.

In a color development, it has been widely known the use of color formers which form color images by the reaction with oxidation products of primary aromatic amino developing agents and there are a number of patents relating thereto. These color formers are coupled with oxidation products of aromatic primary amine to form dyes insoluble in water or the ordinary developer and silver images formed at the same time are removed from the photographic emulsion layer to retain the dye images. These are classified into two types, the one being present in the developer and the other being present in the emulsion layer prior to exposure. The present invention relates to a color former used by addition to a developer. In general, the color forming method thereof is "the substractive color process" and the color former used is the one to obtain cyan, magenta and yellow dyes.

A color former used for color photography is required for forming dyes having desirable spectroscopic absorption characteristics by the color development. The cyan color former should form dyes capable of absorbing completely red light and transmitting completely blue and green light. However, many of color formers which have been employed up to this time are not provided with such characteristics.

On the other hand, in the color development of multilayer color films, it has been well known that while one emulsion layer is developed, undesirable coloring occurs in other emulsion layers by development of fogged grains, which causes remarkable degradation of quality of color reproduction. For example, in the development of a multilayer color film, when it is subjected to reversal exposure by red light after the first development and then treated with a cyan developer containing cyan color former to form cyan images in the red sensitive layer, cyan dye is formed in the magenta forming green sensitive layer and the yellow forming blue sensitive layer. This phenomenon is hereinafter designated as the unfavorable cyan dye formation in other layers. Also, when exposed to white light and treated with a magenta developer containing magenta color former to form magenta images after forming cyan images, magenta dye is formed in the cyan forming layer. This phenomenon is hereinafter designated as the unfavorable magenta dye formation in the cyan layer.

For the purpose of preventing such unfavorable dye

formation, a number of efforts have been made on the processing. In general, however, these two unfavorable color formations are caused by elements opposed each other and this results in such tendency that if the one decreases, the other increases. This problem has not been solved completely yet and rather is a bottleneck to obtain good color reproductions.

It is therefore an object of this invention to provide a cyan color former which can form cyan dyes having excellent spectroscopic absorption characteristic so as to produce pure cyan images and cause little unfavorable cyan dye formation in other layers and unfavorable magenta dye formation in the cyan forming layer. Other objects will appear from the following description and claim. This and other objects are accomplished by the use of 2 - (o - propionamido-β-phenylethyl)-1-hydroxynaphthamide as color former.

As a cyan color former, phenol and naphthol derivatives, particularly 2-β-phenylethyl-1-hydroxynaphthamide derivatives are useful, is well known in the art.

Of these derivatives, the one whose phenyl ring is free from substituted group, that is, 2-β-phenylethyl-1-hydroxynaphthamide and the one whose phenyl ring has substituted group at the para-position, that is, 2-(p-acetamido-β-phenylethyl)-1-hydroxynaphthamide and 2-(p-propionamido-β-phenylethyl)-1-hydroxynaphthamide are not suitable as a cyan color former, since they have not good absorption characteristics. The maximum absorption of the cyan dye formed occurs in a too long wave length and there is much useless absorption at short wave length.

In U.S.P. 3,002,836 is described 2-(o-acetamido-β-phenylethyl)-1-hydroxynaphthamide is a color former capable of forming cyan dyes having a good spectroscopic absorption characteristic. However, it will be understood from the accompanying drawing that the color former of the present invention can form cyan dyes having a much better spectroscopic absorption characteristic. That is to say, in the drawing are shown the spectroscopic absorption curves of the dye image obtained from the oxidation coupling of 2-(o-propionamido-β-phenylethyl)-1 - hydroxynaphthamide and 2 - methyl-4-(N-ethyl-N-2-hydroxyethyl)aminoaniline (A), the dye image obtained from a color former for comparison, 2-(o-acetamido-β-phenylethyl)-1-hydroxy-naphthamide and the same developing agent (B) and the dye image obtained from another color former for comparison, 2-(p-propionamido-β-phenylethyl)-1-hydroxynaphthamide and the same developing agent (C).

It is evident from the drawing that the dye image obtained from the color former used in our invention exhibits a more excellent absorption characteristic, that is, unfavorable absorption near 600 nm. is much less.

It is quite unexpected that in spite of that the color former of our invention, 2-(o-propionamido-β-phenylethyl)-1-hydroxynaphthamide is similar to 2-(o-acetamido-β-phenylethyl)-1-hydroxynaphthamide in the chemical structure, a remarkable difference can be observed between their photographic properties. That is, in accordance with this invention, there is much less unfavorable cyan dye formation in other layers and the unfavorable magenta dye formation in the cyan forming layer, as compared with in the use of 2-(o-acetamido-β-phenylethyl)-1-hydroxynaphthamide as a color former. This is favorable to the photographic color reproduction.

In Table 1 are shown measured values with respect to the unfavorable cyan dye formation in other layers and the unfavorable magenta dye formation in the cyan layer, using the color former of this invention and 2-(o-acetamido-β-phenylethyl)-1-hydroxynaphthamide as a color former.

The degree of the unfavorable cyan dye formation in other layers is represented by a value of cyan color density formed when a multi-layer reversal color film is exposed to red light, then firstly developed by a black and white developer in the conventional manner, subjected to reversal exposure by red light and then to cyan development. The composition of the cyan developer used is as follows:

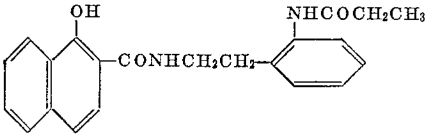
Potassium bromide	g..	1.7
Potassium rhodanate	g..	2.6
Sodium sulfite	g..	10
Sodium carbonate (monohydrate)	g..	23
Monobenzyl-p-aminophenol	g..	1.4
Methanol	ml..	65
Color former, 2-(o-propionamido-β-phenylethyl)-1-hydroxynaphthamide or 2-(o-acetamido-β-phenylethyl)-1-hydroxynaphthamide	g..	1.7
Sodium hydroxide	g..	2.5
Hexylene glycol	ml..	10
2-methyl-4-(N-ethyl-N-2-hydroxyethyl)aminoaniline sulfate	g..	2.8
Water to make 1000 ml.		

The degree of the unfavorable magenta dye formation in the cyan layer is represented by a ratio of the magenta color density to cyan color density, in the case where a film coated with the usual red sensitive emulsion and dried is exposed to red light by the step wedge, developed firstly by a black and white developer in the conventional manner, then subjected to reversal exposure by red light, to cyan development and to magenta development. The composition of the cyan developer used is the same as described above.

TABLE 1

Color former used	Unfavorable cyan dye formation in other layers	Unfavorable magenta dye formation in cyan layer
Color former used in this invention	0.29	0.20
2-(o-acetamido-β-phenylethyl)-1-hydroxynaphthamide	0.38	0.26

The color former used in our invention, 2-(o-propionamido-β-phenylethyl)-1-hydroxynaphthamide having the following structure is prepared by the following procedure:



52 g. of o-aminophenylacetonitrile whose preparation is described in "Journal of the American Chemical Society," vol. 72, p. 3049 was dissolved in 500 ml. of ether with heating, 56.5 g. of propionic anhydride was added thereto and heated for 1 hour with refluxing. Cooling thereof gave white needles. When the thus deposited crystals were collected by filtration and washed with 200 ml. of ether, 61 g. of o-propionamidophenylacetonitrile (yield: 82%) melting at 101–103° C. was obtained.

79 g. of 1-hydroxy-2-naphthoic acid phenyl ester (0.3 mol), 56.5 g. of o-propionamidophenylacetonitrile (0.3 mol), 250 ml. of tert-butyl alcohol and 5 g. of Raney nickel were charged to a 1000 ml. autoclave, to which hydrogen was charged at the initial pressure of 75 kg./cm^2. The mixture was heated at 100° C. and reacted for 3 hours. After cooling to room temperature, 250 ml. of dimethylformamide was added thereto and deposited crystals were heated to dissolve. After filtering nickel, the filtrate was cooled and crystals obtained thereby were washed with 150 ml. of ethyl acetate to give 50 g. of a product (yield: 46%) melting at 218–219° C. Analysis for nitrogen: 7.75% found to 7.73% calculated.

The following examples are illustrative of our invention.

EXAMPLE I

A film coated with the usual red sensitive silver iodobromide emulsion and dried, was exposed to red light by the step wedge, developed for 3 minutes by a black and white developer, subjected to reversal exposure by red light and developed for 5 minutes by a cyan developer, followed by washing with water. This film was subjected to silver bleaching in the conventional manner and fixed by hypo fixer. A positive image of cyan dye was thus obtained. The spectroscopic absorption curve of the color image was shown in the accompanying drawing as "A." The composition of black and white developer and cyan developer are as follows:

Black and white developer:

N-methyl-p-aminophenol sulfate	g..	4.5
Sodium sulfite	g..	70
Hydroquinone	g..	8
Sodium carbonate (monohydrate)	g..	20
Potassium bromide	g..	2.5
Water to make 1000 ml.		

Cyan developer:

Potassium bromide	g..	3
Sodium sulfite	g..	10
Sodium sulfate	g..	50
Potassium rhodanate	g..	1
Monobenzyl-p-aminophenol	g..	0.5
Methanol	ml..	10
p-Aminophenol	g..	0.1
Caustic soda	g..	3
2-(o-propionamido-β-phenylethyl)-1-hydroxynaphthamide	g..	2
Hexylene glycol	ml..	10
2-methyl-4-(N-ethyl-N-2-hydroxyethyl)aminoaniline sulfate	g..	2
Water to make 1000 ml.		

EXAMPLE 2

A film coated with the usual red sensitive silver iodobromide emulsion and dried, was exposed to red light by the step wedge and treated in the similar manner to the Example 1 by the use of the following cyan developer in place of the cyan developer of the Example 1 to obtain a cyan image of cyan dye.

Potassium bromide	g..	2
Sodium sulfite	g..	10
Sodium carbonate (monohydrate)	g..	23
Caustic soda	g..	1.5
2-(o-propionamido-β-phenylethyl)-1-hydroxy-naphthamide	g..	1.5
Hexylene glycol	ml..	10
2-methyl-4-N,N-diethylaminoaniline hydrochloride	g..	3
Water to make 1000 ml.		

EXAMPLE 3

A unusual multi-layer reversal color film of coupler-developer type was exposed, than, was developed for 3 minutes by a black and white developer, washed with water, subjected to reversal exposure by red light and then developed for 4 minutes by a cyan developer. After washing with water and exposure to blue light, it was developed for 4 minutes by a yellow developer. Washed with water, developed for 2 minutes by the black and white developer and washed with water. Then, after exposure to white light, it was subjected to magenta color forming development by a magenta developer. The thus treated film, after washing with water, was subjected to silver bleaching in the conventional manner, fixed by hypo fixer and thereby a photographic color image was obtained.

The composition of the black and white developer was the same as in the Example 1 and that of the cyan, yellow and magenta developers are as follows.

Cyan developing solution:

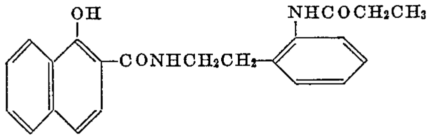
Potassium bromide	g	2
Potassium rhodanate	g	2
Sodium sulfite	g	5
Caustic soda	g	2
2-(o-propionamido-β-phenylethyl)-1-hydroxynaphthamide	g	3
Hexylene glycol	ml	10
2-methyl-4-N,N-diethyl-aminoaniline hydrochloride	g	1.5
Water to make 1000 ml.		

Yellow developing solution:	Grams
Potassium bromide	2
Sodium sulfite	5
Caustic soda	2
Benzoylacetanilide	1.5
4-N,N-diethylaminoaniline sulfate	2
Water to make 1000 ml.	

Magenta developing solution:	Grams
Potassium bromide	2
Sodium sulfite	5
Caustic soda	2
1-phenyl-3-(4-chlorobenzamido)-5-pyrazolone	1.5
2-methyl-4-N,N-diethylaminoaniline hydrochloride	1.5
Water to make 1000 ml.	

We claim:

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



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