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UNITED STATES PATENT OFFICE

2,545,687

N-SUBSTITUTED BENZIMIDAZOLES

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No Drawing. Original application April 30, 1947, Serial No. 745,113. Divided and this application April 16, 1948, Serial No. 21,549. In Canada January 12, 1948

4 Claims. (Cl. 260—309)

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The present invention relates to benzimidazole sulfonic acids having particular utility in color photography for the production of cyan colored images by color forming development. The present application is a division of my copending application Ser. No. 745,113, filed April 30, 1947, entitled "Cyan Color Formers Capable of Yielding Fine Grained Images."

In U. S. P. 2,373,821 there is disclosed cyan color formers comprising an aromatic hydroxy compound containing in its molecule a 5-membered heterocyclic nucleus, such as, a benzothiazole, benzoxazole or benzimidazole. Specific reference is made in the patent to the preparation of 2-(2'-[1'-hydroxy] naphthyl) benzimidazole by heating the condensation product from 1-hydroxy-2-naphthoic acid and o-phenylenediamine to split off water.

The patentee points out that the color formers disclosed therein are particularly characterized by the fact that the dyestuffs obtained therefrom exhibit an especially high absorption in the short wave infra-red, making the color formers eminently suitable for use in the negative-positive process. The patentee also asserts that owing to the high absorption in the long wave red of the quinonimine dyestuffs produced from the color formers, the color formers are also utilizable in the formation of sound records.

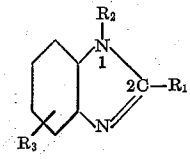
While the color formers described in the patent possess the properties attributable thereto by the patentee, they nevertheless suffer from the very serious disadvantage that the dyestuff images which they yield upon color forming development are of relatively coarse grain. For this reason, such color formers have little or no utility in color film of small size, particularly 8 mm. film which for proper reproduction requires fine grained images, particularly as regards the cyan or key image.

I have now discovered a class of cyan color formers which comprises a hydroxy aromatic radical, the carbon atom in ortho-position to said hydroxyl group being directly linked to the carbon atom in the 2-position of a benzimidazole nucleus, said benzimidazole nucleus being substituted on the nitrogen atom in the 1-position by a long aliphatic chain and in the fused-on benzo radical by a water solubilizing group. It has been ascertained that compounds so constituted, when employed as color formers in photographic emulsions, not only possess the properties of the color formers described in the above mentioned patent but also have the additional very desirable characteristics of yield-

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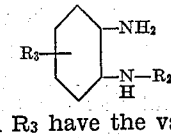
ing cyan dye images on color development which have excellent spectral properties and an exceedingly fine grain. For this reason, the compounds are particularly adapted for utilization in the red sensitive layer of small film such as 8 mm. film which requires exceedingly fine grained images in the cyan or key image layer. Furthermore, because of the presence in the compounds of the long aliphatic chain and the solubilizing substituent, the compounds are readily dispersed in photographic emulsions and are non-migratory once they have been incorporated therein. Said color formers, their use in photographic emulsions, and the processing of such emulsions to cyan dye images, constitute the purposes and objects of the present invention.

The color formers contemplated herein are depicted by the following structural formula:



wherein R_1 is a hydroxy aromatic radical, the hydroxy group being directly linked to a nuclear carbon atom, such as hydroxy naphthyl, hydroxy phenyl and the like, and such radicals substituted by halogen, i. e., chlorine, bromine and the like, sulfo, carboxy, lower alkyl, i. e., alkyl containing up to five carbon atoms, such as methyl, ethyl, propyl, butyl and amyl, and lower alkoxy, the alkyl radical of which is as above, R_2 is a long aliphatic chain containing at least ten carbon atoms, such as decyl, lauryl, oleyl, octadecyl and the like, and R_3 is a water solubilizing group, such as sulfo, carboxy, hydroxy, hydroxy polyethenoxy ether radical, and the like.

The new class of color formers is obtained by two reactions, the first involving the condensation of 1-hydroxy-2-aroyl chloride with an ortho-phenylenediamine of the following formula:

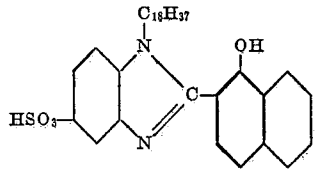


wherein R_2 and R_3 have the values given above with the elimination of hydrogen chloride, and the second involving the ring closure of the condensation product with elimination of water. The condensation reaction is generally effected by heating the components in an inert diluent, such as benzene, toluene or the like to a tem-

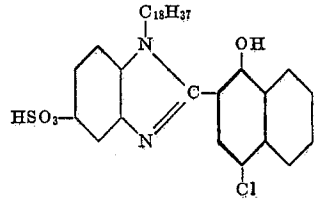
perature ranging from about 75 to 150° C. in the presence of an acid binding agent, such as pyridine, α-picoline, quinoline, and the like. The ring closure reaction is generally effected by heating the condensation product to a temperature ranging from about 100 to 135° C. in the presence of a water binding agent, such as acetic anhydride, glacial acetic acid and the like. The product resulting from ring closure after isolation from the reaction mixture may be purified by dissolving it in a hot mixture of benzene and alcohol and recrystallizing the product from such solution.

The following are illustrative of color formers embraced by the above class:

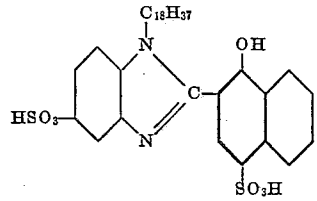
(1) 1-octadecyl-2-(2' - (1 - hydroxy) naphthyl) benzimidazole-5-sulfonic acid.



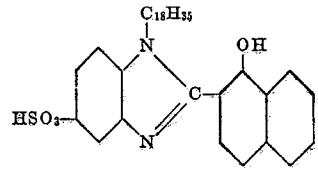
(2) 1-octadecyl-2-(2'-(1'-hydroxy - 4' - chloro) naphthyl) benzimidazole-5-sulfonic acid.



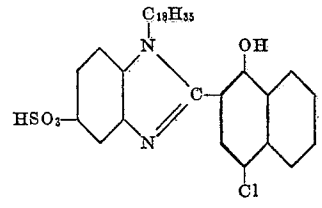
(3) 1 - octadecyl-2-(2'-(1'-hydroxy - 4' - sulfo) naphthyl) benzimidazole-5-sulfonic acid.



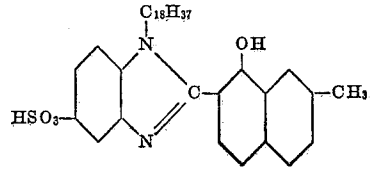
(4) 1-oleyl-2-(2'-(1'-hydroxy) naphthyl) benzimidazole-5-sulfonic acid.



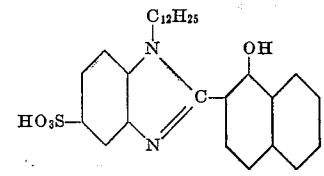
(5) 1-oleyl-2-(2'- (1'- hydroxy-4'-chloro) naphthyl) benzimidazole-5-sulfonic acid.



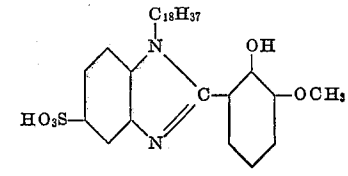
(6) 1-octadecyl-2-(2'-(1'-hydroxy - 6' - methyl) phenyl) benzimidazole-5-sulfonic acid.



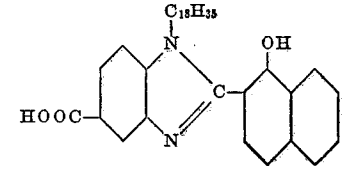
(7) 1-lauryl-2(2'-(1'-hydroxy) naphthyl)-benzimidazole-5-sulfonic acid.



(8) 1-octadecyl - 2(2'-(1'- hydroxy-6'- methoxy) phenyl) benzimidazole-5-sulfonic acid.



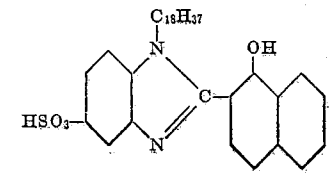
(9) 1-oleyl-2-(2'-(1-hydroxy) naphthyl) benzimidazole-5-carboxylic acid.



The color formers are incorporated in photographic emulsions in the customary manner as by dissolving them in water or aqueous alkaline solutions and adding the solution to a gelatino silver halide emulsion. The emulsions may be utilized for the production of colored negatives, reversed positives or in the negative positive process.

The following examples serve to further illustrate the invention but it is to be understood that the invention is not restricted thereto. The parts are by weight unless otherwise stated.

Example 1



50 parts of 3-amino-4-octadecylaminobenzene sulfonic acid are suspended in 500 parts of benzene containing 30 parts of pyridine. After distilling off 100 parts of benzene to remove water, there are added at 65–70° C. 30 parts of 1-hydroxy-2-naphthoyl chloride.

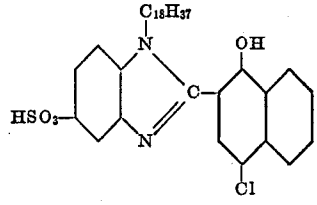
The benzene is removed by distillation at 80° C. to 100° C. over a period of 1 hour. The reaction mixture is heated from 100° C. to 130° C. over a period of 1 hour, and maintained at 130–135° C. for 2 hours. To the residue is added at 120° C. 250 parts of glacial acetic acid. After heating at 115–120° C. for ½ hour and cooling below 80° C., there are added 150 parts ethanol or methanol. The mixture is cooled to 20° C. and agitated for 2 to 5 hours. After chilling at 0–5° C. for 1 hour, the crude product is collected on a filter, washed with 200 parts of ethanol, sucked dry, then air dried.

The crude product is recrystallized by dissolving it in a refluxing mixture of 350 parts of benzene, and 150 parts of ethanol. The solution is filtered while hot to remove any insoluble material.

The filtrate is cooled to 20° C., agitated for ½ hour and then chilled at 15° C. for ½ hour. The crystalline product is collected on a filter, washed with 125 parts of ethanol, sucked dry and then air dried. .5 gram of the resulting color former is added to 100 cc. of a photographic silver bromide emulsion. The emulsion is coated on a transparent support and dried. After exposure, the film is developed in a color forming developer comprising water,
1000 parts of sodium sulfite,
15 parts of p-diethylamino aniline,
2.5 parts of sodium carbonate and
70 parts of potassium bromide.

A silver+ dye image is formed. After removal of the silver by bleaching in a potassium ferrocyanide solution and subsequent fixing a deeply colored greenish blue dye image remains, said dye image being characterized by an exceedingly fine grain.

Example 2

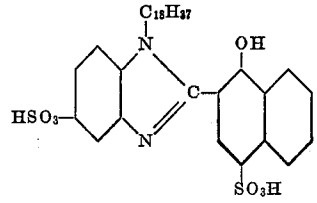


This product is prepared by the same method used in Example 1 but from

50 parts of 3-amino-4-octadecylaminobenzenesulfonic acid,
500 parts of benzene,
30 parts of pyridine, and
42 parts of 1-hydroxy-4-chloro-2-naphthoyl chloride.

When this color former is incorporated in a photographic silver halide emulsion, the emulsion coated on a support and exposed, developed and processed as in Example 1, beautiful cyan dye images of exceedingly fine grain are obtained.

Example 3



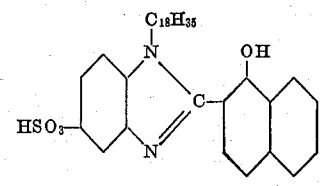
To 250 parts of sulfuric acid (100%) at 10° C. are added portionwise 50 parts of 1-octadecyl-2-(2'-(1'-hydroxy) naphthyl) benzimidazole-5-sulfonic acid.

The reaction mixture is agitated at 10–15° C. for 1 hour, then warmed to 20–25° C. and agitated until sulfonation is complete. After drowning in 2000 parts of ice with agitation, there are added 1000 parts of water, and 300 parts of potassium chloride. The crude product is collected on a filter, washed with 10% KCl solution, and dried.

The product is purified by recrystallization from 500 parts of methanol.

This color former when used in photographic silver halide emulsions likewise yields cyan dye images of excellent spectral properties and exceedingly fine grain.

Example 4

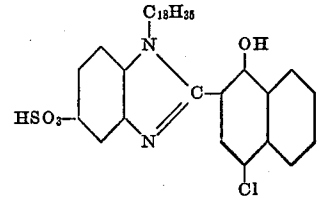


This product is prepared in the same manner as that of Example 1 but from

45 parts of 3-amino-4-oleylaminobenzenesulfonic acid,
300 parts of pyridine,
110 parts of benzene, and
40 parts of 1-(carbethoxy-hydroxy)-2-naphthoyl chloride.

This color former gives on color forming development with the developer of Example 1 cyan dye images of exceedingly fine grain.

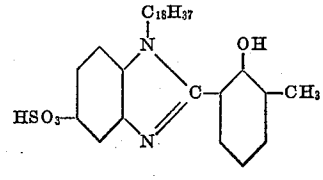
Example 5



This product is prepared in the same manner as that of Example 1 but from

50 parts of 3-amino-4-oleylaminobenzenesulfonic acid,
350 parts of pyridine,
100 parts of benzene, and
35 parts of 1-hydroxy-4-chloro-2-naphthoyl chloride.

Example 6



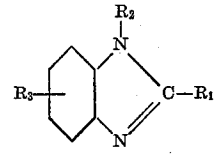
This product is prepared in the same manner as that of Example 1 but from

44 parts of 3-amino-4-octadecylaminobenzenesulfonic acid,
450 parts of benzene,
25 parts of pyridine, and
30 parts of beta-cresotinoyl chloride.

Color formers of Examples 5 and 6 likewise yield on development with the developer of Example 1 cyan dye images of exceedingly fine grain and excellent spectral properties.

I claim:

1. Compounds of the following formula:



wherein R_1 is a hydroxy aromatic radical, the hydroxy group being nuclear attached, and said radical being linked to the benzimidazole radical in ortho-position to said hydroxy group, R_2

is an aliphatic hydrocarbon radical containing at least ten carbon atoms and R_3 is a water solubilizing group.

2. 1-octadecyl-2-(2'-(1' - hydroxy) naphthyl) benzimidazole-5-sulfonic acid.

3. 1-octadecyl-2-[2'-(1'-hydroxy-4' - chloro)-naphthyl]-benzimidazole-5-sulfonic acid.

4. 1-oleyl-2 - [2' - (1' - hydroxy) - naphthyl]-benzimidazole-5-sulfonic acid.

WINFRED C. CRAIG.

REFERENCES CITED

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

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