

1

3,099,559

SILVER-FREE COLOR REPRODUCTION PROCESS AND COMPOSITION THEREFOR

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16 Claims. (Cl. 96-48)

This invention relates to color photography. More particularly, this invention relates to a color process involving the production of hardened, colored gelatin relief images.

It is known that gelatin can be hardened by prolonged exposure to various types of radiations such as ultraviolet light or visible radiation. It is likewise known that the hardening of gelatin by radiation may be accelerated by incorporating in the gelatin certain inorganic compounds such as dichromates, i.e., sodium or potassium dichromate, metallic silver and the like. If the aforesaid radiation constitutes an optical image such as would be obtained by superimposing a pattern between the radiation source and the gelatin layer, then hardening is proportional to the intensity of the exposing radiation with the result that a hardened gelatin image is obtained. The unexposed and, therefore, unhardened gelatin portions can be removed, such as by washing, thereby leaving a hardened gelatin relief image. The image can be colored or used for the production of planographic prints.

An important application of the hardening of gelatin is in the field of color photography wherein colored images of hardened gelatin are placed in register in order to reproduce the color aspects of a subject. In this process, a colored image is formed by developing a reducible silver salt image in the presence of a compound which couples during the development with the oxidation product of the developing agent and forms a dyestuff which deposits on the developed silver grains. After the metallic silver image is removed, a dyed gelatin image remains which is then hardened with a hardening agent such as formaldehyde, dichromate or the like.

In the aforesaid method of producing colored images of dyed, hardened gelatin, it is necessary to use a light sensitive silver halide emulsion in conjunction with a color forming component as the photographic element. Drawbacks of such photographic elements are the need for expensive light sensitive silver halide emulsion and complex manufacturing facilities and equipment.

It has now been discovered that colored photographic dye images of hardened gelatin can be produced without recourse to expensive light sensitive silver halide emulsions and the provision of such dye images constitute the objects and purposes of this invention.

In accordance with the present invention, I produce a colored photographic image of hardened gelatin by irradiating gelatin in the presence of certain color couplers or color forming components characterized by the presence of a salt forming group followed by dyeing of the hardened gelatin in the exposed areas. In practicing the invention, I prefer to coat, on a suitable base or support, a mixture of aqueous gelatin and color coupler. The resulting photographic element comprising a base and light sensitive layer thereon of gelatin and color former is then exposed through a pattern to the radiations emanating from an ultraviolet lamp. The so exposed coating is then immersed in a p-N,N-dialkylaminoaniline type color developer solution for a few minutes and then contacted with a solution of an oxidizing agent such as potassium ferrocyanide. As a result of the aforesaid treatment, indiscriminate color coupling occurs throughout the film. The coating is then developed by washing

2

in warm water which treatment removes the unhardened gelatin plus dye in the unexposed areas leaving a dyed, hardened gelatin image corresponding to the areas exposed to radiation.

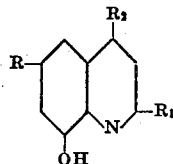
If desired, the exposure may be carried out using visible light in which case the time of exposure required to effect hardening is somewhat longer.

Other oxidizing agents of a type commonly employed in the photographic art can be used in lieu of the potassium ferrocyanide and in this connection mention is made of such materials as ammonium and alkali metal persulfates, organic peroxides, metal perchlorates and the like. In fact, it has been my experience that any type of oxidizing agent can be used for the purpose of practicing the invention provided it does not have a destructive action on the hardened gelatin or the dye used in forming the colored image.

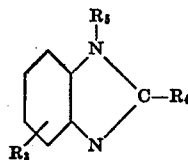
Color development of the hardened gelatin image can be achieved by means other than by the coupling reaction between the oxidation products of p-phenylenediamine color developers and the color coupling component. Thus, in place of a color developer, there may be substituted diazonium salts, aldehydes, sulfo hydrazides and the like, all of which react with the color coupler to produce a colored dye. Furthermore, these compounds, unlike the p-phenylenediamine color developers, do not require the presence of an oxidizing agent since they react directly with the color forming component.

The color forming components of the type suitable for practicing the invention are depicted by the following general formulae:

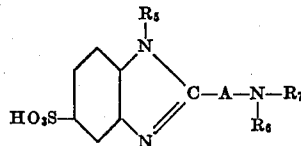
I



II



III



In Formula I, R is halogen, i.e., bromine, chlorine, iodine or the like, nitro, sulfo, or an arsonic acid radical, R1 is hydrogen, alkyl or a mononuclear carbocyclic aromatic radical such as phenyl, nitrophenyl, aminophenyl, stearylaminophenyl, octadecanesulfoamidophenyl, chlorophenyl, tolyl, anisyl and the like, R2 is hydrogen, —COOH or —CONHR8 and R8 is a sulfonated aliphatic radical containing at least 10 carbon atoms or a sulfonated aromatic radical substituted by an aliphatic radical containing at least 10 carbon atoms.

In Formula II, R4 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, R5 is a long aliphatic chain containing at least ten carbon atoms, such as,

3

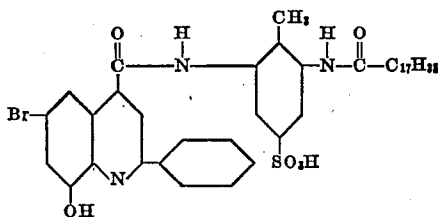
decyl, lauryl, oleyl, octadecyl and the like and R_3 is a water solubilizing group, such as, sulfo, carboxy, hydroxy, hydroxy polyethenoxy ether radical and the like.

In Formula III, R_5 has the value given above, R_6 is hydrogen or aliphatic acyl, e.g., acetyl, propionyl, butyryl, valeryl, capronyl, heptanoyl, caproyl, pelargonyl, undecyl, lauroyl, myristoyl, stearoyl, etc., R_7 represents a J-acid radical and A represents an arene radical, i.e., p-phenylene, 1,4-naphthalene, etc.

Examples of compounds of the type embraced by 10 Formula I are the following:

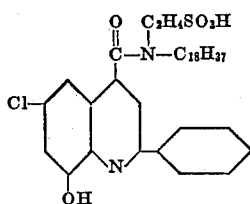
COMPOUND 1

6-Stearoylamino-2-(2-Phenyl-6-Bromo-8-Hydroxycinchoninoyl)Aminotoluene-4-Sulfonic Acid



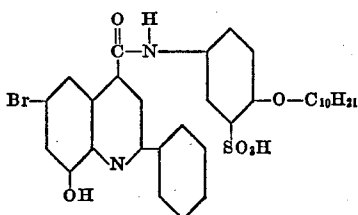
COMPOUND 2

2-Phenyl-6-Chloro-8-Hydroxycinchoninoyloctadecyltaurine



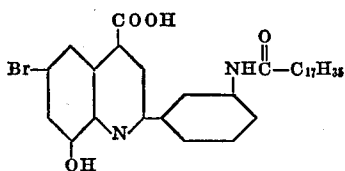
COMPOUND 3

6-Decoxy-3-(2-Phenyl-6-Bromo-8-Hydroxycinchoninoyl)Aminobenzenesulfonic Acid



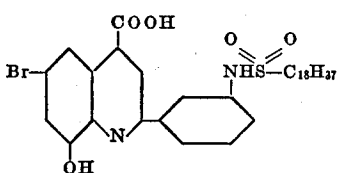
COMPOUND 4

2-(3-Stearoylamino-phenyl)-6-Bromo-8-Hydroxycinchoninic Acid



COMPOUND 5

2-(3-Octadecanesulfonamidophenyl)-6-Bromo-8-Hydroxycinchoninic Acid

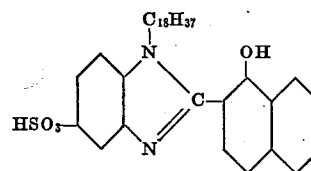


Examples of compounds of the type included under Formula II are the following:

4

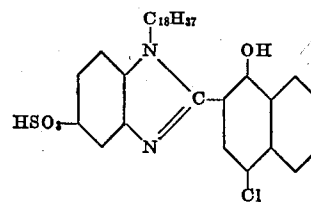
COMPOUND 6

1-Octadecyl-2-(2'-(1'-Hydroxy)Naphthyl)Benzimidazole-5-Sulfonic Acid



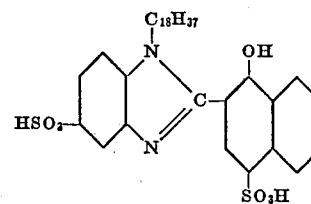
COMPOUND 7

1-Octadecyl-2-(2'-(1'-Hydroxy-4'-Chloro)Naphthyl)Benzimidazole-5-Sulfonic Acid



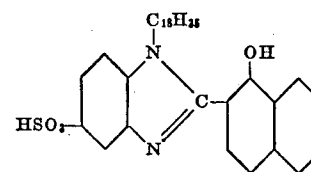
COMPOUND 8

1-Octadecyl-2-(2'-(1'-Hydroxy-4'-Sulfo)naphthyl)Benzimidazole-5-Sulfonic Acid



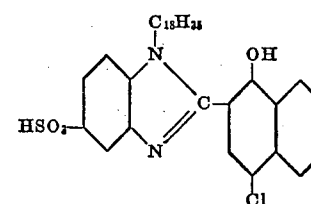
COMPOUND 9

1-Oleyl-2-(2'-(1'-Hydroxy)Naphthyl)Benzimidazole-5-Sulfonic Acid



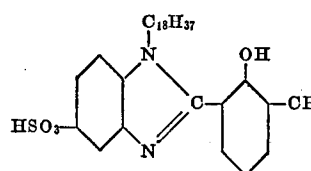
COMPOUND 10

1-Oleyl-2-(2'-(1'-Hydroxy-4'-Chloro)Naphthyl)Benzimidazole-5-Sulfonic Acid



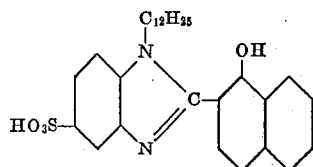
COMPOUND 11

1-Octadecyl-2-(2'-(1'-Hydroxy-6'-Methyl)Phenyl)Benzimidazole-5-Sulfonic Acid



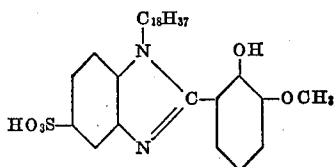
5
COMPOUND 12

1-Lauryl-2-(2'-(1'-Hydroxy)Naphthyl)Benzimidazole-5-Sulfonic Acid



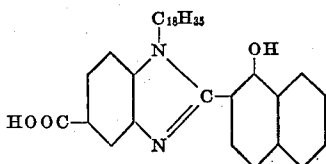
COMPOUND 13

1-Octadecyl-2-(2'-(1'-Hydroxy-6'-Methoxy)Phenyl)Benzimidazole-5-Sulfonic Acid



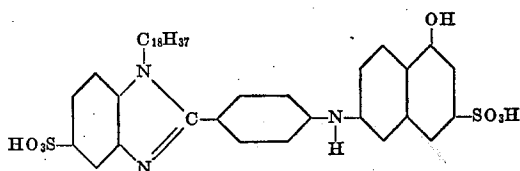
COMPOUND 14

1-Oleyl-2-(2'-(1'-Hydroxy)Naphthyl)Benzimidazole-5-Carboxylic Acid

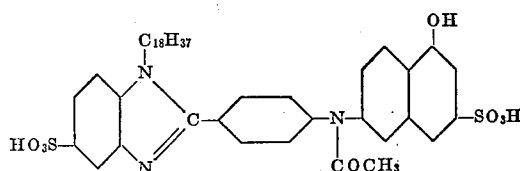


Examples of compounds of the type included within the ambit of Formula III are the following:

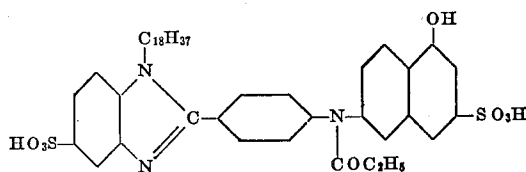
COMPOUND 15



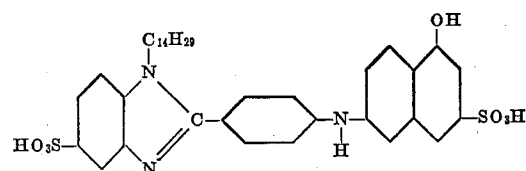
COMPOUND 16



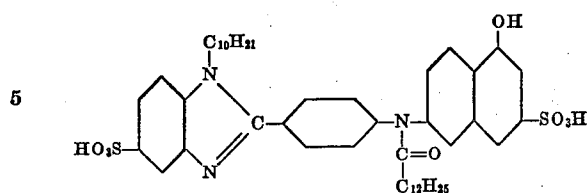
COMPOUND 17



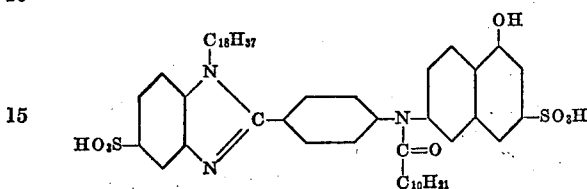
COMPOUND 18



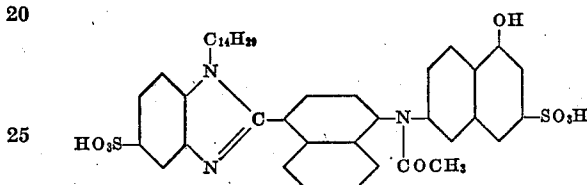
6
COMPOUND 19



COMPOUND 20



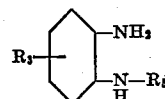
COMPOUND 21



It is to be noted that the aforelisted color couplers contain a long aliphatic chain, the purpose of which is to prevent diffusion or migration of such compounds when they are incorporated in a multilayer photographic element.

For the most part, the color couplers disclosed herein are known compounds and their preparation and properties are given in the chemical literature. Thus, compounds of Formulae I and II are referred to respectively in U.S. Patents 2,524,741 and 2,530,349.

Couplers of the type embraced by formula III, while not specifically referred to in the literature, can be prepared by conventional methods known to the art. These compounds can be synthesized by reacting a 4'-carboxyaryl-J-acid with an o-phenylenediamine of the following formula:



wherein R_3 and R_5 have the values given above, the method used being generally that disclosed in the aforementioned U.S. Patent 2,530,349. The carboxyaryl-J-acids are described in U.S.P. 2,591,642.

The p-phenylenediamine color developers, the oxidation products of which are used to couple with the couplers as set forth herein, are so well known in the photographic art that it is considered unnecessary to describe these materials in detail.

I have also ascertained that azine developing agents can also be used for practicing my invention. The azine developing agents are aromatic triamines which on color development with appropriate couplers give rise to phenazonium dyestuff images. Such color developers are also well known in the art and in this connection reference is made to the following U.S. patents: 2,486,440, 2,522,802, 2,569,906, 2,570,116, 2,537,460.

In some instances, it may be undesirable to use an oxidizing agent in which case the p-phenylenediamine or azine developing agents can be replaced by an aromatic diazonium compound in order to form a colored image by coupling with a color forming component in order to produce the colored, hardened gelatin images. Such aromatic diazonium compounds usually employed in the form of their stable diazonium sulfates, chlorobenzene sulfates, chlorfluorides, etc., are known chemical compounds. In general, such diazonium compounds are prepared by diazotization of aromatic amines by the well known pro-

7

cedure of diazotizing the particular amine with sodium nitrite in the presence of an acid. For a comprehensive treatise on the diazotization of aromatic amines, reference is made to *The Aromatic Diazo Compounds and Their Technical Applications*, 2nd edition, 1949, by Saunders.

The method of producing hardened gelatin images as described herein is compatible with ancillary gelatin hardening agents and I have, in fact, ascertained that my hardening process can be augmented by such well known gelatin hardeners as the alkali metal dichromates, silver, silver salts and the like.

My method of forming colored, hardened gelatin images is eminently suitable for reproducing the colored aspects of a subject. Thus, a light sensitive photographic element, prepared in accordance with the present invention, is exposed to one of the primary colored aspects of a subject as represented for instance by a color separation negative or positive. The resulting exposed and hardened gelatin image is then subtractively dyed and developed in accordance with the methods set forth above. Similarly prepared photographic elements are then exposed to the remaining color aspects of the subject and dyed with the appropriate subtractive dye. The resulting subtractively dyed color aspects are then placed in register which is then viewed through a white light source in order to reconstruct the complete color aspects of the subject.

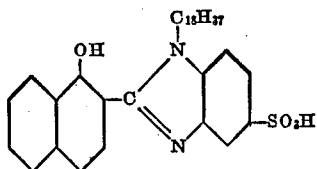
In place of making physically separate coatings for each primary color aspect of the subject as above, a single photographic element can be used to record the color aspects of the subject. In this method, a photographic element is prepared by the previous method and exposed and the image of hardened gelatin subtractively dyed to one of the color aspects of the subject. After removal of the unhardened gelatin in the non-irradiated areas, the same photographic element is given a second coating, exposed, subtractively dyed in order to record a second primary color aspect of the subject. The process of coating, exposing and dyeing is then repeated until all of the remaining color aspects of the subject have been reproduced. In this manner, all of the colors of the subject are thus recorded on a single layer. This method has the advantage that once the color aspects are recorded, the problem of keeping three physically separate reproductions in register is eliminated.

My colored, hardened photographic images can be formed on a wide variety of surfaces including transparent, translucent and opaque supports such as ceramic ware, paper, glass, plastic, etc.

The following examples are given in order to illustrate the invention in greater detail. It is to be understood, however, that these examples are given by way of illustration only and are not to be taken as limiting the invention.

EXAMPLE I

1 gram of the compound



was dissolved in 100 ml. of 3% gelatin and coated on a white opaque support to yield a coating of approximately 2-6 M. The coating thus obtained was exposed through a pattern such as a silver negative to ultraviolet radiation emanating from the lamp in a White Print Machine at slow speed (4 passes). The resulting exposed coating was then treated in the following manner:

A. A section of the coating was immersed in a p-N,N-dialkylaminoaniline type color developer solution for 1-2 minutes. This was followed by immersing the coating in a potassium ferricyanide oxidizing bath for several minutes. As a result of this treatment, an indiscriminant

8

color coupling occurred throughout the film. The coating was then bathed in warm water (40-50° C.). The unhardened gelatin plus dye in the unexposed areas was thus removed by washing and a positive blue-green dye plus gelatin image remained in the areas exposed to radiation.

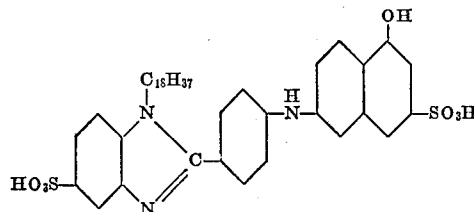
B. A section of the exposed coating was bathed in a solution of diazotized sulfanilic acid which was adjusted to a pH of about 6 with acetic acid. Color coupling again occurred indiscriminantly to yield a red dye. The processed coating was then washed as before to yield a positive red azo dye plus gelatin image in the regions hardened by exposure.

The color developer formulation used above had the following composition:

2-amino-5-diethylaminotoluene	g--	2
Sodium carbonate (anhydrous)	g--	20
Sodium sulfite (anhydrous)	g--	2
Potassium bromide	g--	0.2
Water to make	liter--	1

EXAMPLE II

A coating was made in the manner described in Example I with the exception that instead of the hardening compound used therein a hardening compound having the formula



was used. The film was exposed as in Example I and the exposed coating was treated in the following manner:

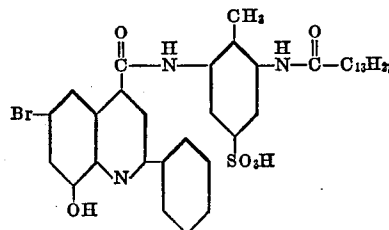
A. A section of the exposed coating was immersed in a color developing solution containing a 6-phenylamino-4-dimethylaminometanilic acid type as a color developer. The coating was then processed in a ferricyanide oxidizing bath as before to yield an overall blue-green azine dye. The processed strip was then washed as in Example I to yield a positive hardened gelatin plus blue-green azine dye in the exposed areas of the film.

B. A section of the exposed film was bathed in diazotized sulfanilic acid and treated as in Example IB to yield a reddish magenta azo positive dye image.

The developer formulation used above was the same as given in Example I of U.S.P. 2,522,802 except that an equivalent amount of 6-phenylamino-4-dimethylaminometanilic acid was used in place of the developing agent of the example of the patent.

EXAMPLE III

A coating was prepared as in Example I using the hardening compound



instead of the hardening compound of Example I. The material was then treated as in Example IIA. A magenta azine dye image was produced.

EXAMPLE IV

The same procedure was employed as in Example IA and B except that the material was cast on transparent film base. The material may thus be exposed through the base rather than the gelatin. This procedure gives

9

the greatest hardening in the gelatin next to the base which promotes better adhesion of the hardened gelatin to the base.

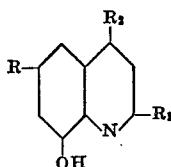
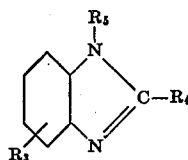
EXAMPLE V

A coating of 0.5 g. of 3-(1'-hydroxy-2-naphthoyl) N'-octadecylamidoisophthalic acid and 0.5 g. of sodium dichromate in 100 ml. of 3% gelatin was coated on transparent film base. The material was exposed through the base and developed as in Example I. In this case, a bluish-green dye image is obtained with p-phenylenediamine type developer and an orange with diazotized sulfanilic acid.

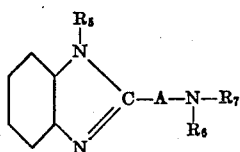
My invention is not limited to the detailed description thereof contained herein, but includes all modifications that fall within the scope of the appended claims.

I claim:

1. A radiation sensitive photographic element comprising a base and a radiation sensitive coating thereon, said coating being free of silver halide and consisting essentially of gelatin and a color coupler selected from those represented by the following general formulae:



and



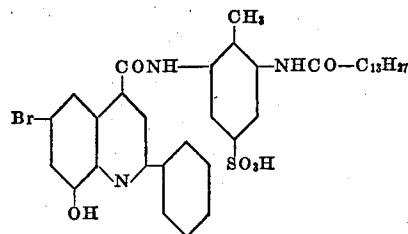
wherein R is a member selected from the class consisting of halogen, nitro, sulfo and arsonic acid radicals, R₁ is a member selected from the class consisting of hydrogen, alkyl and a mononuclear carbocyclic aromatic radical, R₂ is a member selected from the class consisting of H, —COOH and —CONH—R₃ and R₃ is a member selected from the class consisting of sulfonated aliphatic radicals containing at least 10 carbon atoms and sulfonated aromatic radicals substituted by an aliphatic radical containing at least 10 carbon atoms; R₄ is an hydroxy aromatic radical, the hydroxy group being nuclearly attached and said radical being linked to the benzimidazole radical in the ortho position to said hydroxy group, R₅ is a long aliphatic chain capable of rendering said compound fast to diffusion in a photographic colloid, R₆ is a member selected from the class consisting of hydrogen and aliphatic acyl radicals, R₇ represents a J-acid radical and —A— is an arylene group selected from the class consisting of a p-phenylene radical and a naphthylene radical.

2. The product as recited in claim 1 wherein the base is transparent.

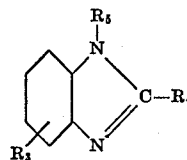
3. The product as recited in claim 1 wherein the base is opaque.

10

4. The product as recited in claim 1 wherein the coupler is represented by the following formula:

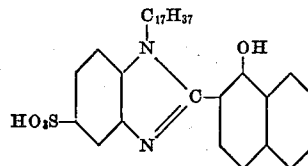


5. The product as recited in claim 1 wherein the color coupler is represented by the following general formula:

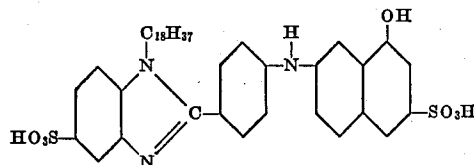


wherein R₃ is a water solubilizing group, R₄ is an hydroxy aromatic radical, the hydroxy group being nuclearly attached and said radical being linked to the benzimidazole radical in the ortho position to said hydroxy group, R₅ is a long aliphatic chain capable of rendering said compound fast to diffusion in a photographic colloid.

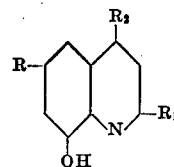
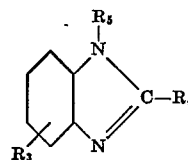
6. The product as recited in claim 5 wherein the color coupler is represented by the following formula:



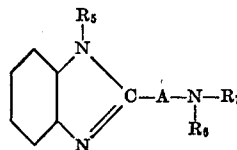
7. The product as recited in claim 1 wherein the color coupler is represented by the following formula:



8. A method of producing a hardened gelatin colored photographic reproduction which comprises exposing to an optical image a radiation sensitive photographic element comprising a base and a radiation sensitive coating thereon, said coating consisting essentially of gelatin and a color coupler selected from those represented by the following general formulae:



and



11

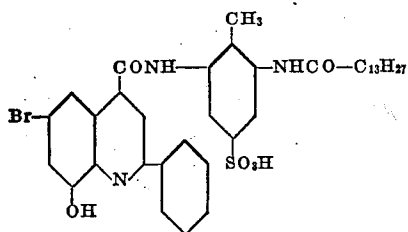
wherein R is a member selected from the class consisting of halogen, nitro, sulfo and arsonic acid radicals, R₁ is a member selected from the class consisting of hydrogen, alkyl and a mononuclear carbocyclic aromatic radical, R₂ is a member selected from the class consisting of H, —COOH and —CONH—R₈ and R₈ is a member selected from the class consisting of sulfonated aliphatic radicals containing at least 10 carbon atoms and sulfonated aromatic radicals substituted by an aliphatic radical containing at least 10 carbon atoms; R₃ is a water solubilizing group, R₄ is a hydroxy aromatic radical, the hydroxy group being nuclearly attached and said radical being linked to the benzimidazole radical in the ortho position to said hydroxy group, R₅ is a long aliphatic chain capable of rendering said compound fast to diffusion in a photographic colloid, R₆ is a member selected from the class consisting of hydrogen and aliphatic acyl radicals, R₇ represents a J-acid radical and —A— is an arylene group selected from the class consisting of a p-phenylene radical and a naphthylene radical, hardening by said exposure the gelatin layer in the exposed areas treating the exposed photographic element with a primary aromatic amino color developer in the presence of a water soluble oxidizing agent in order to effect color coupling between the said color coupler and said color developer, removing by washing the unexposed and unhardened gelatin in the unexposed areas of the coating thereby leaving a colored, hardened gelatin relief image corresponding to the exposed areas.

9. The process as defined in claim 8 wherein the base is transparent.

10. The process as defined in claim 8 wherein the base is opaque.

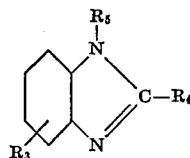
11. The process as defined in claim 8 wherein the p-phenylenediamine color developer contains in the position ortho to the free amino group an amino group having at least one free hydrogen.

12. The process as defined in claim 8 wherein the coupler is represented by the following formula:



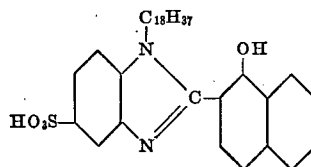
12

13. The process as defined in claim 8 wherein the color coupler is represented by the following general formula:

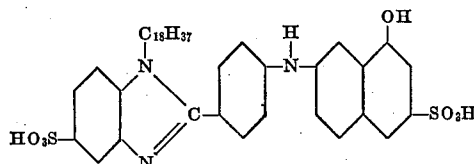


wherein R₃ is a water solubilizing group, R₄ is a hydroxy aromatic radical, the hydroxy group being nuclearly attached and said radical being linked to the benzimidazole radical in the ortho position to said hydroxy group, R₅ is a long aliphatic chain capable of rendering said compound fast to diffusion in a photographic colloid.

14. The process as defined in claim 13 wherein the color coupler is represented by the following formula:



15. The process as defined in claim 8 wherein the color coupler is represented by the following formula:



16. The method as defined by claim 8 wherein the light used in exposing the photographic element to an optical image is provided by an ultraviolet light source.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

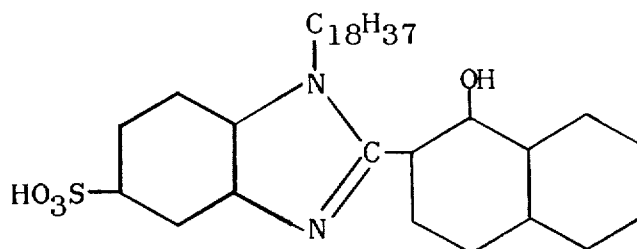
Patent No. 3,099,559

July 30, 1963

Robert F. Coles

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, "COMPOUND 2", in the heading, for "Hydrocinchoninoyleoctadecyltaurine", in italics, read -- Hydroxycinchoninoyleoctadecyltaurine --, in italics; column 6, line 39, for "to" read -- in --; column 9, line 52, for "form" read -- from --; column 10, lines 31 to 38, the formula should appear as shown below instead of as in the patent:



column 12, line 43, for "2,426,984" read -- 2,426,894 --.

Signed and sealed this 16th day of June 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents