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COLOR TURBIDITY AGENT IN COLOR PHOTOGRAPHIC MATERIALS

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U.S. Cl. 96—100 32 Claims

ABSTRACT OF THE DISCLOSURE

By incorporating vinylmethylimidazol homopolymer or copolymer into a photographic layer, such as a silver halide emulsion layer, a protective layer, a filter layer or an antihalation layer, color turbidity of a coupler-containing color photographic silver halide material is prevented.

The present invention relates to color photography and more particularly to an incorporated coupler type color photographic material containing a color turbidity preventing agent.

There has been known several types of color photographic materials containing in the photographic emulsion layers color couplers that form dye-images by coupling with the oxidation products of a N,N-dialkyl-p-phenylenediamine type developing agents.

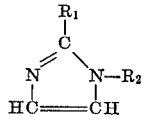
In one type of them, a coupler having an oil-soluble group is dissolved in a high boiling point oily solvent, and the solution is then dispersed in a gelatin solution containing a dispersing agent such as sodium alkylbenzene sulfonate, and then a mixture of thus prepared dispersion and a photographic emulsion is coated upon a suitable support.

In another type of them, an oil-soluble coupler in melt or in the form of solution in a low-boiling organic solvent is mixed with a photographic emulsion without using any water-immiscible high boiling point organic solvent followed by coating on a support.

In still another type of them, a water-soluble or an alkali-soluble group is introduced into a coupler having the long chain aliphatic hydrocarbon group and the coupler is incorporated in the form of alkaline solution in a photographic emulsion followed by coating on a suitable support.

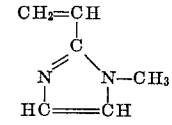
In such a type of color photographic materials, there frequently occur such troubles that the color of the dye-images become turbid, the purity of the color is reduced. Hereinafter, such a reduction of the color purity of color saturation is called "color turbidity". It is because of the fact that the process of removing developed sliver by an oxidation bleaching bath after color development is often incompletely carried out and a part of the developed silver remains unoxidized. The spectrally broad light absorption band of the silver thus appears over the sharp light absorption band of the dye-image.

The inventors have found that by incorporating in a color photographic element particularly in a color photographic emulsion containing an oil-soluble coupler and a high boiling point oily solvent a polymer of vinyl-methylimidazol having the following structure

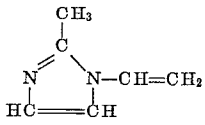


(wherein R_1 and R_2 each represents $CH_2=CH-$ or CH_3- and they are different from each other) or a copolymer of it with other monomer, the silver removing process is easily carried out to completion and the color turbidity of the dye image can be reduced.

The vinylmethylimidazole mentioned above is, in other words, 2-vinyl-1-methylimidazol having the structure



or 1-vinyl-2-methylimidazol having the structure



In this case, the binding agent for the color photographic emulsion may be a suitably protective colloid, such as, gelatin, polyvinyl alcohol, a derivative thereof, polyacrylamide, a derivative thereof, a cellulose derivative, casein, and an alginate, but gelatin is most preferable.

The polymer used in this invention is a 2-vinyl-1-methylimidazol polymer of a polymer of 1-vinyl-2-methylimidazol, or a copolymer containing the above-mentioned vinyl-methylimidazol. The monomer to be copolymerized with the vinylmethylimidazol in this invention may be vinyl ester, acrylic acid ester, methacrylic acid ester, acrylamide, a derivative thereof, methacrylamide, a derivative thereof, acrylic acid, methacrylic acid, styrene, styrene sulfonic acid, vinyl pyrrolidone and the like. As the vinyl ester, there are vinyl acetate, vinyl propionate, vinyl butyrate and the like. As the acrylic ester, there are methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, etc. As the acrylamide derivative may be N-methylacrylamide, N-ethylacrylamide, N-propylacrylamide, N-butylacrylamide, N,N-diethylacrylamide, acryloil morpholine and the like. The methacrylamide derivative may be N-methylmethacrylamide, N-ethylmethacrylamide, methacryloil morpholine and the like.

For example, in the case of copolymer of the vinyl methylimidazol and vinyl acetate, the copolymer gives the best effect when the monomer molecular ratio is 7:3 but the copolymer having other monomer molecular ratio may be effectively used in this invention if it contains the vinyl methylimidazol. The polymer and the copolymer of the vinyl methylimidazol in this invention may be used alone or a mixture thereof.

The polymer or the copolymer used in this invention may be soluble in an alkaline solution or miscible in water in colloid state but more preferably be soluble in organic solvents.

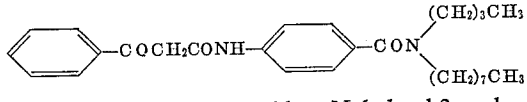
The effect of the above-mentioned polymer or copolymer is not substantially influenced by the polymerization degree and the polymer of any polymerization degree may be used in this invention if it is soluble in the above-mentioned solvents, liquid having high boiling point (at least above 200° C.) or solid. However, the transparency of the highlight portion of picture is better as the polymerization degree is higher.

The organic solvent utilized for dissolving the polymer or the copolymer in a photographic emulsion may be alcohols, such as, methanol, ethanol, isopropanol, etc.; ether alcohols, such as, Cellosolve, carbithols, etc.; esters, such as, ethyl acetate, butyl acetate, etc.; ethers, such as, ethyl-ether, dioxane, tetrahydrofuran, etc.; ketones, such as, acetone, methylethyl ketone, etc.; amides, such as, lactams, dialkyl carbamides, etc.; and the like.

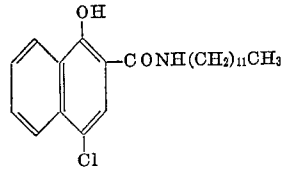
The mixing ratio of the polymer in a photographic emulsion is varied by the kind and amount of the coupler in the emulsion. In general, the optimum amount of the polymer is in the order of 5% by weight based on the weight of gelatin present in the emulsion but the content may of course be larger than the value. However, since the coupling efficiency to dye-forming development and the physical properties of the film are lowered if the amount of the polymer is higher than 25%, a suitable mixing amount is generally about 5 to about 12%.

The invention may be applied effectively to any couplers used in color photographic elements but particularly good results are obtained when it is used with the following oil-soluble couplers.

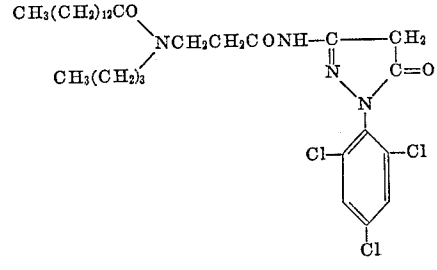
Coupler 1.—4-benzoylacetamido-N-butyl-N-octyl-benzamide



Coupler 2.—1-hydroxy-4-chloro-N-dodecyl-2-naphthamide



Coupler 3.—1-(2,4,6-trichlorophenyl)-3-(3-(N-butyltetradecanamido)-propanamido)pyrazoline-5-on



The color turbidity preventing polymer or copolymer in this invention may be added at dispersing the coupler, at mixing the dispersion in a photographic emulsion, or at coating the emulsion on a support, but the addition at dispersing the coupler is most preferable. Moreover, in this invention, the color turbidity preventing polymer or copolymer may be added in at least one of subsidiary layers of the color photographic element, such as, an antihalation layer, an insulating layer, a filter layer, a protective layer, and the like as the case may be, whereby the color turbidity of the adjacent emulsion layer can be prevented. In this case, the polymer or the copolymer gives remarkable effect when added in an amount more than 5% by weight and may be added into the subsidiary layers in an amount up to about 75% by weight of the gelatin without giving any bad influences on the physical properties of film and coupling efficiency.

The invention will further be explained more in detail by the following examples.

Example 1

Into a mixture of 1.2 ml. of dibutyl phthalate and 3.0 ml. of ethyl acetate was dissolved 4.0 g. of the above-mentioned Coupler 1 by heating and the solution was added into 10 ml. of a 10% aqueous gelatin solution containing 0.8 g. of a copolymer of 2-vinyl-1-methylimidazol and acrylamide (monomer ratio 7:3 and 2.0 ml. of a 10% aqueous solution of sodium alkylbenzene sulfonate and the mixture was homogenized with a high speed for 3 minutes at 40–50° C. by means of a homo blender five times with intervals of 1 minute each to prepare a dispersion of the coupler, the polymer and gelatin.

Thus prepared dispersion was added in a gelatino silver halide emulsion containing 4.5 g. of silver bromide and 7.5 g. of gelatin. After coating the emulsion on a film base, the emulsion layer was exposed and subjected to color treatments, such as, color development, water washing, potassium ferricyanide-bromide bleaching treatment, etc. Since a yellow coupler was used in this example, the degree of the turbidity of dye-image was determined by measuring the optical density with red filter. The results are shown in the following table.

TABLE 1

2-vinyl-1-methylimidazol-acrylamide copolymer, monomer ratio 7:3

	Red optical density
Not contained	0.79
Contained	0.38

The optical density value shows that by incorporating the copolymer of 2-vinyl-1-methylimidazole and acrylamide in the color photographic emulsion layer, the turbidity (the value of optical density in the wavelength region of no dye absorption) is reduced.

Example 2

A color photographic emulsion that had been prepared by the same manner as in Example 1 using 0.8 g. of a 2-vinyl-1-methylimidazol instead of the copolymer in Example 1 was coated on a film base and, after exposure, was subjected to color treatments, such as, color development, water-washing, potassium ferricyanide-bromide bleaching treatment, etc. Since a yellow coupler was used in this example, the turbidity value was determined by measuring the red optical density value. The value is 0.21.

Example 3

The same procedure as in Example 1 was repeated using a 2-vinyl-1-methylimidazol-acrylic acid copolymer (monomer ratio 7:3) instead of the copolymer in Example 1. The turbidity value was 0.28 in red optical density value.

Example 4

The same procedure as in Example 1 was repeated using a 2-vinyl-1-methylimidazol-vinyl acetate copolymer (monomer ratio 7:3). The turbidity value was 0.29 in red optical value.

Example 5

The same procedure as in Example 1 was repeated using a 2-vinyl-1-methylimidazol-vinyl pyrrolidone copolymer (monomer ratio 7:3). The turbidity value was 0.34 in red optical value.

Example 6

A color photographic element was prepared as in Example 1 using 2.40 g. of Coupler 2 instead of the coupler in Example 1. The photographic element was exposed and subjected to color treatments, such as color development, water-washing and potassium ferricyanide-bromide bleaching. In the case of using a cyan coupler as in this example, the cyan turbidity can be determined by measuring the blue optical density value. The results are shown in the following table.

TABLE 2

2-vinyl-1-methylimidazol-acrylamide copolymer (monomer ratio 7:3)

Coupler 2 (cyan):	Blue optical density
Not contained	0.91
Contained	0.51

Example 7

A color photographic element was prepared as in Example 1 using 4.30 g. of Coupler 3 instead of the coupler in Example 1. The element was exposed and subjected to color treatments, such as color development, water-washing, and potassium ferricyanide-bromide bleaching. In the case of using a magenta coupler as in this example, the magenta turbidity value can be determined by measuring the red optical density value. The results are shown in the following table.

TABLE 3

2-vinyl-1-methylimidazol-acrylamide copolymer (monomer ratio 7:3)

Coupler 3 (magenta):	Red optical density
Not contained	0.63
Contained	0.39

Example 8

A coating solution of 0.80 g. of 2-vinyl-1-methylimidazol-acrylamide copolymer (monomer ratio 7:3) in 100 g. of an aqueous 3% (by weight) gelatin solution was coated as an intermediate layer upon a red-sensitive silver halide emulsion layer containing the cyan coupler. Thus prepared photographic elements was exposed and subjected to color treatments, such as, color development, water-washing, and potassium ferricyanide-bromide bleaching. The turbidity value of the cyan coupler-containing layer is shown in the following table in blue optical density value.

TABLE 4

2-vinyl-1-methylimidazol-acrylamide copolymer (monomer ratio 7:3)

Coupler 2 (cyan):	Blue optical density
Not contained	0.91
Contained	0.68

Example 9

The same procedure as in Example 1 was repeated using a 1-vinyl-2-methylimidazol-acrylamide copolymer (monomer ratio 7:3). The turbidity value was 0.35 in red optical density value.

Example 10

A 1-vinyl-2-methylimidazol polymer was used instead of the copolymer in Example 1. The turbidity value was 0.25 in red optical density value.

Example 11

A 1-vinyl-2-methylimidazol-acrylic acid copolymer (monomer ratio 7:3) was used instead of the copolymer in Example 1. The turbidity value was 0.31 in red optical density value.

Example 12

A 1-vinyl-2-methylimidazol-vinyl acetate copolymer (monomer ratio 7:3) was used instead of the copolymer in Example 1. The turbidity value was 0.28 in red optical density value.

Example 13

A 1-vinyl-2-methylimidazol-vinyl pyrrolidone copolymer (monomer ratio 7:3) was used instead of the copolymer in Example 1. The turbidity value was 0.37 in red optical density value.

Example 14

A color photographic element was prepared as in Example 1 using 2.40 g. of Coupler 2 instead of the coupler in Example 1. The element was exposed and subjected to color treatments, such as, color development, water-washing, and potassium ferricyanide-bromide bleaching. In the case of using cyan coupler as in this example, the cyan turbidity can be determined by measuring the blue optical density value. The results are shown in the following table.

TABLE 5

1-vinyl-2-methylimidazol-acrylamide copolymer (monomer ratio 7:3)

Coupler 2 (cyan):	Blue optical density
Not contained	0.91
Contained	0.41

Example 15

A color photographic element was prepared by the same manner as in Example 1 using 4.30 g. of Coupler 3 instead of the coupler in Example 1. The photographic element was exposed and subjected to color development, water-washing, and potassium ferricyanide-bromide bleaching. In the case of using a magenta coupler as in this example, the magenta turbidity was determined by measuring the red optical density value. The results are shown in the following table.

TABLE 6

1-vinyl-2-methylimidazol-acrylamide copolymer (monomer ratio 7:3)

Coupler 3 (magenta):	Red optical density
Not contained	0.63
Contained	0.43

Example 16

A coating solution of 0.80 g. of a 1-vinyl-2-methylimidazol-acrylamide copolymer (monomer ratio 7:3) in 100 g. of an aqueous 3% (by weight) gelatin solution was coated as an intermediate layer upon a red-sensitive silver halide layer containing the cyan coupler. Thus prepared photographic element was exposed and subjected to color treatments, such as, color development, water-washing, and potassium ferricyanide-bromide bleaching. The turbidity value of the cyan coupler is shown in the following table in blue optical density value.

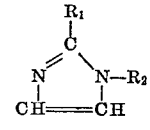
TABLE 7

1-vinyl-2-methylimidazol-acrylamide copolymer (monomer ratio 7:3)

Coupler 2 (cyan):	Blue optical density
Not contained	0.91
Contained	0.63

What is claimed is:

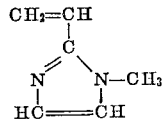
1. A color photographic gelatino silver halide material comprising a support and at least one photographic gelatino silver halide emulsion layer containing a color coupler, and at least one of said layers containing a polymer material selected from the group consisting of a polymer of the vinylmethylimidazol shown by the general formula.



(wherein R_1 and R_2 each represents a member selected from the group consisting of $CH_2{=}CH{-}$ and $CH_3{-}$, said R_1 and R_2 being different from each other and a copolymer of said vinylmethylimidazol and a monomer selected from the group consisting of vinyl ester, acrylic acid ester, methacrylic acid ester, acrylamide, a derivative of acrylamide, methacrylamide, a derivative of methacrylamide, acrylic acid, methacrylic acid, styrene, styrene sulfonic acid, and vinyl pyrrolidone.

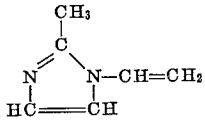
2. The color photographic silver halide material as claimed in claim 1, wherein said polymer material is se-

lected from a polymer of 2-vinyl-1-methylimidazol shown by the formula



and a copolymer thereof with a monomer selected from the group consisting of vinyl ester, acrylic acid ester, methacrylic acid ester, acrylamide, a derivative of acrylamide, a derivative of methacrylamide, acrylic acid, methacrylic acid, styrene, styrene sulfonic acid and vinyl pyrrolidone.

3. The color photographic silver halide material as claimed in claim 1, wherein said polymer material is selected from a polymer of 1-vinyl-2-methylimidazol shown by the formula



and a copolymer thereof with a monomer selected from the group consisting of vinyl ester, acrylic acid ester, methacrylic acid ester, acrylamide, a derivative of acrylamide, methacrylamide, a derivative of methacrylamide, acrylic acid, methacrylic acid, styrene, styrene sulfonic acid and vinyl pyrrolidone.

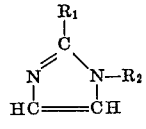
4. The color photographic silver halide material as claimed in claim 1 wherein said polymer material is in said photographic emulsion layer and the amount of said polymer material in the emulsion layer is 5 to 25 percent by weight based on the amount of gelatin in the emulsion layer.

5. The color photographic silver halide material as claimed in claim 1 wherein said coupler is 4-benzoyl-acetamido-N-octylbenzamide.

6. The color photographic silver halide material as claimed in claim 1 wherein said coupler is 1-hydroxy-4-chloro-N-dodecyl-2-naphthamide.

7. The color photographic silver halide material as claimed in claim 1 wherein said coupler is 1-(2,4,6-trichlorophenyl)-3-(3 - (N - butyltetradecanamido) - propanamido)-pyrozoline-5-on.

8. A color photographic gelatino silver halide material comprising a support, at least one photographic gelatino silver halide emulsion layer containing an oil soluble color coupler, an antihalation layer, an intermediate layer, a filter layer, and a protective layer, at least one of said layers containing a polymer material selected from the group consisting of a polymer of the vinylmethylimidazol shown by the general formula

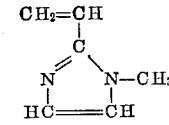


wherein R_1 and R_2 each represents a member selected from the group consisting of CH_2=CH— and CH_3—, said R_1 and R_2 being different from each other and a copolymer of said vinylmethylimidazol and a monomer selected from the group consisting of vinyl ester, acrylic acid ester, methacrylic acid ester, acrylamide, a derivative of acrylamide, methacrylamide, a derivative of methacrylamide, acrylic acid, methacrylic acid, styrene, styrene sulfonic acid, and vinyl pyrrolidone.

9. The color photographic silver halide material according to claim 8, wherein the coupler forms dye-images by coupling with the oxidation product of a N, N-dialkyl-p-phenylene-diamine type developing agent.

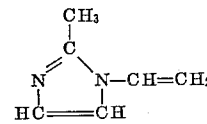
10. The color photographic silver halide material as claimed in claim 8, wherein said polymer material is

selected from a polymer of 2-vinyl-1-methylimidazol shown by the formula



and a copolymer thereof with a monomer selected from the group consisting of vinyl ester, acrylic acid ester, methacrylic acid ester, acrylamide, a derivative of acrylamide, methacrylamide, a derivative of methacrylamide, acrylic acid, methacrylic acid, styrene, styrene sulfonic acid and vinyl pyrrolidone.

11. The color photographic silver halide material as claimed in claim 8, wherein said polymer material is selected from a polymer of 1-vinyl-2-methylimidazol shown by the formula



and a copolymer thereof with a monomer selected from the group consisting of vinyl ester, acrylic acid ester, methacrylic acid ester, acrylamide, a derivative of acrylamide, methacrylamide, a derivative of methacrylamide, acrylic acid, methacrylic acid, styrene, styrene sulfonic acid and vinyl pyrrolidone.

12. The color photographic silver halide material as claimed in claim 8 wherein said polymer material is in said photographic emulsion layer and the amount of said polymer material in the emulsion layer is 5 to 25 percent by weight based on the amount of gelatin in the emulsion layer.

13. The color photographic silver halide material as claimed in claim 8 wherein said coupler is 4-benzoyl-acetamido-N-octylbenzamide.

14. The color photographic silver halide material as claimed in claim 8 wherein said coupler is 1-hydroxy-4-chloro-N-dodecyl-2-naphthamide.

15. The color photographic silver halide material as claimed in claim 8 wherein said coupler is 1-(2,4,6-trichlorophenyl) - 3 - (3 - N - butyltetradecanamido)-propanamido)-pyrozoline-5-on.

16. The color photographic silver halide material as claimed in claim 8 wherein at least one of said layers contains 5 to 75 percent by weight based on the amount of gelatin of the polymer material.

17. The color photographic silver halide material as claimed in claim 9 wherein said copolymer is a 2-vinyl-1-methylimidazol-acrylamide copolymer.

18. The color photographic silver halide material as claimed in claim 9 wherein said copolymer is a 2-vinyl-1-methylimidazol-acrylic acid copolymer.

19. The color photographic silver halide material as claimed in claim 9 wherein said copolymer is a 2-vinyl-1-methylimidazol-vinyl acetate copolymer.

20. The color photographic silver halide material as claimed in claim 9 wherein said copolymer is a 2-vinyl-1-methylimidazol-vinyl pyrrolidone copolymer.

21. The color photographic silver halide material as claimed in claim 10 wherein said copolymer is a 2-vinyl-1-methylimidazol-acrylamide copolymer.

22. The color photographic silver halide material as claimed in claim 10 wherein said copolymer is a 2-vinyl-1-methylimidazol-acrylic acid copolymer.

23. The color photographic silver halide material as claimed in claim 10 wherein said copolymer is a 2-vinyl-1-methylimidazol-vinyl acetate copolymer.

24. The color photographic silver halide material as claimed in claim 11 wherein said copolymer is a 2-vinyl-1-methylimidazol-vinyl pyrrolidone copolymer.

25. The color photographic silver halide material as

claimed in claim **3** wherein said copolymer is a 1-vinyl-2-methylimidazol-acrylamide copolymer.

26. The color photographic silver halide material as claimed in claim **3** wherein said copolymer is a 1-vinyl-2-methylimidazol-acrylic acid copolymer.

27. The color photographic silver halide material as claimed in claim **3** wherein said copolymer is a 1-vinyl-2-methylimidazol-vinyl acetate copolymer.

28. The color photographic silver halide material as claimed in claim **3** wherein said copolymer is a 1-vinyl-2-methylimidazol-vinyl pyrrolidone copolymer.

29. The color photographic silver halide material as claimed in claim **11** wherein said copolymer is a 1-vinyl-2-methylimidazol-acrylamide copolymer.

30. The color photographic silver halide material as claimed in claim **11** wherein said copolymer is a 1-vinyl-2-methylimidazol-acrylic acid copolymer.

31. The color photographic silver halide material as claimed in claim **11** wherein said copolymer is a 1-vinyl-2-methylimidazol-vinyl acetate copolymer.

32. The color photographic silver halide material as claimed in claim **11** wherein said copolymer is a 1-vinyl-2-methylimidazol-vinyl pyrrolidone copolymer.

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U.S. Cl. X.R.

96—84, 87, 114