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MULTILAYERED COLOR PHOTOGRAPHIC MATERIAL

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U.S. Cl. 96—74 22 Claims

ABSTRACT OF THE DISCLOSURE

A multilayered color photographic material having increased viscosity and coagulation temperature at application and having excellent permeability of treating solution at development and providing good hard film after fixing can be obtained by incorporating a styrene/maleic anhydride copolymer and/or a condensation reaction product of said copolymer and polyvinyl alcohol in gelatin.

The present invention relates to a multilayered color photographic material obtained according to a process in which is used an emulsion prepared by dissolving a water-insoluble or slightly water-soluble coupler in a high boiling solvent, dispersing the solution by means of a colloid mill or the like in gelatine in the presence of a surface active agent and redispersing the resulting dispersion in a silver halide emulsion. The development of such a multilayered color photographic material involves not only the step for reduction of the silver halide but also the step for coupling of the coupler with an oxidation product of developing agent which is formed at the time of reduction of the silver halide, and as disclosed in British Pat. 834,186 (1960), the effect on color density of such solvent for oil-soluble coupler in the developer as benzyl alcohol, n-octyl alcohol, p-n-amylphenol, p-cresol or the like is so great that it is necessary that the said developer components should sufficiently diffuse and penetrate down into the lowermost layer of the multilayered color photographic material. Accordingly, the hardness of each emulsion layer greatly affects the color development conditions, and such a lower molecular hardener as formalin, which has heretofore been used as a hardener for gelatine photographic emulsions, markedly injure the storage stability of this kind of multilayered color photographic material due to the so-called after-hardening action thereof. In order to improve the stability of photographic materials, various improvements have been made with respect to hardeners. However, substantially all of such hardeners are not comparable in hardening effect to formalin, and have such drawbacks that the resulting films swell on the surfaces at the time of dry-glazing or adhere to dry-glazing plates.

With an aim to overcome the above-mentioned difficulties, the present inventors made extensive studies to find the facts that a film formed by use of a gelatine-silver halide emulsion containing a styrene-maleic anhydride copolymer or a condensation reaction product thereof with polyvinyl alcohol is excellent, as compared with the case of gelatine alone, in permeability for such developer components as alkali, developing agent and solvent, e.g. benzyl alcohol, and that during the color development treatment comprising the steps of development, fixing, bleaching, hardening-fixing and stabilization, the film is successfully hardened particularly when treated with such an inorganic hardener as chromium alum or potassium alum at the hardening-fixing step, and even a film low in hardness at the development step becomes successfully applicable to a dry glazing plate, with the

result that the color development conditions can be made advantageous.

That is, a multilayered color photographic material, in which the gelatine used has been partly substituted by the styrene-maleic anhydride copolymer in accordance with the present invention, is markedly improved in film hardness after the hardening-fixing step, even when the film hardness is relatively low at the development step, whereby an image favorable in the applicability to dry-glazing plate can be obtained. The substitution ratio of the styrene-maleic anhydride copolymer is preferably in the range of 2% to 40%. If the ratio becomes more than 40%, there is brought about such disadvantage that the white background of the photographic material is yellowed due to deposition of the developing agent. In the case of a condensate of the styrene-maleic anhydride copolymer and polyvinyl alcohol the condensation ratio of the former to the latter is desirably in the range of 1:5 or less by weight. If the proportion of polyvinyl alcohol is made greater than that indicated above, there are caused such drawbacks that the condensate is lowered in compatibility with gelatine, and the hardening effect on the film at the hardening treatment step is decreased. The above-mentioned condensed polymer is desirably substituted in an amount of 2 to 40% based on the amount of the gelatine. If the amount of the condensed polymer is less than 2%, the effect is low, while if the amount thereof is more than 40%, the hardening effect at the hardening step becomes excessive, whereby the film becomes brittle and tends to form cracks.

The present invention not only display excellent features in permeability for developer components and in hardening effect at the fixing treatment, as mentioned above, but also solves various problems of the prior art in the steps for production of multilayered color photographic materials, particularly in the coating treatment of light-sensitive emulsions, as mentioned below.

That is, a so-called protective (oil-soluble) coupler is water-insoluble or slightly water-soluble and, in order to disperse said coupler in a gelatine-silver halide photographic emulsion, there is adopted such a process that the coupler is dissolved in a high boiling solvent, e.g. dibutyl phthalate or tricresyl phosphate, the resulting solution is dispersed by means of a colloid mill or the like in an aqueous gelatine solution in the presence of a surface active agent, and then the thus formed dispersion is redispersed in the silver halide emulsion. This process, however, has such drawbacks as mentioned below. That is, when the coupler dispersion is added to the silver halide emulsion, the gelatine is deteriorated in physical properties and the coagulation temperature of the emulsion is greatly lowered. Further, depending on the kind and amount of the oil used, the emulsion is lowered in viscosity to bring about such difficulties in the production of photographic material that the flow of the emulsion is caused at the time of the coating or the swelling of the resulting film is caused at the drying step. In view of the above, various viscosity-increasing agents have been examined, but most of these agents are low in effect of increasing the coagulation temperature of the emulsion, though they can increase the viscosity thereof, or give adverse effects when viewed from the standpoint of photography, and viscosity-increasing agents, which are favorable in setting property and successfully usable in photography, have scarcely been found.

The above-mentioned difficulties may be overcome if the gelatine concentration of the photographic emulsion is increased. However, in the case of a multilayered color photographic material, the development conditions of the lower-most layer are greatly deteriorated with increasing thickness of each coating film to make it extremely difficult to obtain a well-balanced excellent photographic material. Accordingly, in order to make closer as far as possible the development conditions of the upper-most layer to those of the lower-most layer, it is desirable that each coating film is made as thin as possible. Thus, there is also a limit in increasing the gelatine concentration of the photographic emulsion.

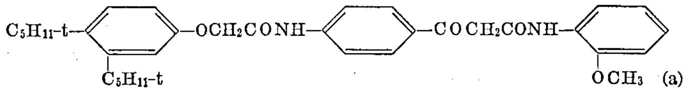
In accordance with the present invention, there have been obtained such extremely desirable results that the viscosity of a photographic emulsion containing an oil-soluble coupler is increased by substituting a part of the gelatine by a styrene-maleic anhydride copolymer or a condensation reaction product thereof with polyvinyl alcohol; that when the thus treated emulsion is coated on a support and then dried, the emulsion is greatly increased in viscosity and becomes difficultly flowable to bring about such effect that the coagulation temperature thereof has substantially been increased, and thus the emulsion can be uniformly coated on a support without increasing the thickness of the resulting film; and that the emulsion film containing the aforesaid polymer is more excellent in permeability for developer components and is more increased in photographic speed than an emulsion containing only gelatine. According to the above-mentioned viewpoint, preferably 2% to 40%, more preferably 5% to 15% of the gelatine is substituted when the styrene-maleic anhydride copolymer is used alone. As the substitution ratio increases, the viscosity-increasing effect becomes greater, but when the substitution ratio becomes more than 40%, the photographic properties of the resulting color photographic material are deteriorated, conversely. This is considered ascribable to the fact that as compared with gelatine, the said polymer is high in buffering action to pH and hence lowers the development conditions. The condensation reaction product of styrene-maleic anhydride copolymer and polyvinyl alcohol is prepared by using each component at a purity as high as possible. The polymerization degree of the polyvinyl alcohol is preferably 500 to 1,000. The reaction conditions should be controlled depending on the blending ratio and molecular weights of the two components and the pH and temperature of the liquid. The blending ratio of styrene-maleic anhydride to polyvinyl alcohol is preferably from 1:0.5 to 1:4. If the proportion of the polyvinyl alcohol becomes great, the condensate is deteriorated in compatibility with the gelatine. The substitution ratio of the gelatine is preferably 2 to 40%, more preferably 5 to 15%, whereby more favorable results can be obtained.

When the copolymer and the condensation product are jointly used, the amount of sum of them is also preferably 2 to 40%.

The present invention is illustrated in further detail below with reference to examples.

EXAMPLE 1

(1)

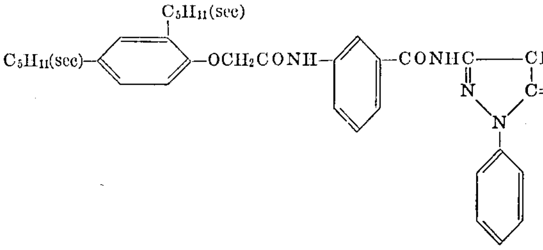


(a)

4 g. of a yellow coupler of the above Formula a and 8 ml. of ethyl acetate were dissolved in 8 ml. of dibutyl phthalate, and the resulting solution was dispersed with stirring at a high speed by means of a homogeneous blender in 100 ml. of 5% gelatine containing 10 cc. of 5% saponin. The thus obtained dispersion was mixed with a gelatin-silver halide emulsion containing 5 g. of silver bromide and 8 g. of gelatin. Subsequently, the emulsion was coated on a formalin-incorporated baryta paper so that the amount of the coupler became 1.0 g./m.^{2}. The emulsion contained no hardener. (Yellow layer.)

(2) On the thus formed layer, a 3% gelatin solution was coated to form a layer of about 1.5 in thickness. In this case, Formalin was used as a hardener in an amount of 2% based on the amount of the gelatin.

(3)



(b)

2 g. of a magenta coupler of the above Formula b was dissolved at an elevated temperature in a mixture comprising 2 ml. of tricresyl phosphate and 10 ml. of ethyl acetate, and the resulting solution was dispersed by means of a homogeneous blender in 40 ml. of 10% gelatin containing 4 ml. of 10% sodium dodecylbenzenesulfonate. The resulting dispersion was redispersed in a green-sensitizing dye-incorporated gelatin emulsion containing 4.5 g. of ordinary silver chlorobromide and 16 g. of gelatin. Subsequently, the emulsion was charged with a stabilizer and saponin, and then coated on the layer formed in the preceding step (2) so that the amount of the coupler in the resulting layer became 0.5 g./m.^{2}. The emulsion contained no hardener. (Magenta layer.)

(4) On the thus formed layer, a 3% gelatin solution (incorporated with formalin in an amount of 1% based on the amount of the gelatin) was further coated so as to form a layer of about 1.5μ in thickness.

(5) 3 g. of the cyan coupler 1-hydroxy-2-naphthoyloctylamide was dissolved in a mixture comprising 3 ml. of diethyl phthalate and 5 ml. of ethyl acetate, and the resulting solution was dispersed in 100 ml. of 5% gelatin in the same manner as in the foregoing step (3). The resulting dispersion was added to a red-sensitized ordinary chlorobromide emulsion. This cyan emulsion contained 4 g. of silver halide and 15 g. of gelatin. The emulsion was charged with a stabilizer and saponin and then coated on the layer formed in the preceding step (4) so that the amount of the coupler became 0.4 g./m.^{2}. The emulsion contained no hardener. (Cyan layer.)

(6) On the thus formed layer, a 4% gelatin solution was coated so as to form a layer of 2.0μ in thickness. As a hardener, formalin was used in an amount of 2% based on the amount of the gelatin.

In the above manner, a multilayered color photographic printing paper (sample A) was prepared as a control.

On the other hand, the same procedures as above were repeated, except that the gelatin in the yellow, magenta and cyan emulsions was substituted by the styrene-maleic anhydride copolymer of the present invention in such proportions as set forth below.

Yellow layer: 3% of the gelatin was substituted.
Magenta layer: 5% of the gelatin was substituted.
Cyan layer: 10% of the gelatin was substituted.

The thus obtained multilayered color photographic printing paper (sample B) did not differ in thickness from the control. Moreover, the sample B was somewhat lower in hardness of crude printing paper than the sample A.

Each of the samples A and B was exposed and then subjected to ordinary color development treatment using a color developer of the following composition:

COLOR DEVELOPER

2-methyl-4-N,N-diethylaminoaniline	g	3.0
Sodium sulfite	g	3.0
Caustic soda	g	1.0
Sodium carbonate (monohydrate)	g	20.0
Borax	g	5.0
Hydroxylamine sulfate	g	2.0
Potassium bromide	g	1.0
Benzyl alcohol	ml	3.0

Water to make 1,000 ml.

Subsequently, each sample was bleached and fixed by use of a bleaching solution and a hardening-fixing solution of the compositions set forth below to remove undeveloped silver halide and reduced silver formed.

BLEACHING SOLUTION

	G.
Red prussiate	90
Potassium bromide	20

Water to make 1,000 ml.

HARDENING-FIXING SOLUTION

Hypo	g	180
Sodium sulfite	g	20
20% acetic acid	ml	55
Potassium alum	g	30
Boric acid	g	20

Water to make 1,000 ml.

After each treatment, the sample was thoroughly washed with water.

The samples after treatments were individually passed to a dry-glazing plate. As the result, the sample A was dissolved on the surface and adhered to the dry-glazing plate. On the other hand, the sample B was low in film hardness, like the sample A, when it was in the development and bleaching steps. However, after immersion in the hardening-fixing solution, the sample B became extremely high in film hardness and, even when passed to a dry-glazing plate kept at 80° C., it did not adhere to the plate and gave a printed image excellent in applicability to the dry-glazing plate.

EXAMPLE 2

In place of the styrene-maleic anhydride copolymer of Example 1, there was used a condensed polymer prepared in the following manner:

Polyvinyl alcohol (polymerization degree 500)	g	50
Styrene-maleic anhydride copolymer	g	50
Water	ml	700

The above-mentioned components were dissolved together at an elevated temperature, and the resulting solution was adjusted to pH 4.0 and heated with stirring at 95° C. for 5 hours. After cooling the solution to room temperature, the total amount was made 800 g. and the pH was controlled.

Using the thus prepared condensed polymer, the gelatin in the yellow, magenta and cyan layers of Example 1 was substituted in such proportions as set forth below.

Yellow layer: 5% of the gelatin was substituted.
Magenta layer: 3% of the gelatin was substituted.
Cyan layer: 20% of the gelatin was substituted.

The thus obtained multilayered color photographic printing paper was low in film hardness during the color development treatment, whereby the color development conditions were made advantageous. After the hardening treatment, the printing paper became extremely high in hardness and was favorable in applicability to dry-glazing plate. Thus, the color photographic printing paper obtained in the above manner was markedly excellent from the practical standpoint.

EXAMPLE 3

A multilayered color photographic printing paper was prepared in the same manner as in Example 1, except that the gelatine in the yellow, magenta and cyan layers was partly substituted by the polymers set forth below.

10% of the gelatin in the yellow layer was substituted by the condensed polymer of Example 2.
3% of the gelatin in the magenta layer was substituted by the styrene-maleic anhydride copolymer.
10% of the gelatine in the cyan layer was substituted by a condensed polymer prepared in the following manner:

Polyvinyl alcohol (polymerization degree 500)	g	20
Polyvinyl alcohol (polymerization degree 1,000)	g	10
Styrene-maleic anhydride copolymer	g	20
Water	ml	700

The above-mentioned components were dissolved together at an elevated temperature, and the resulting solution was adjusted to pH 4.5 and heated with stirring at 98° C. for 4 hours. After cooling the solution to room temperature, the total amount was made 800 g.

The thus obtained multi-layered color photographic printing paper was low in film hardness at the time of color development, but became extremely high in film hardness by the subsequent hardening treatment and gave an excellent color image favorable in applicability to dry-glazing plate.

EXAMPLE 4

3 g. of the cyan coupler 1-hydroxy-2-naphthoyloctylamide was dissolved in 4.5 g. of dibutyl phthalate, and the resulting solution was dispersed by means of a colloid mill in 80 ml. of 2% gelatin in the presence of saponin. The resulting dispersion was added to a chlorobromide-gelatin emulsion containing 4 g. of silver halide. The thus treated emulsion was charged according to an ordinary procedure with sensitizing dye, stabilizer and activator, and the total amount was made 590 g. to prepare a control emulsion. The gelatin concentration of the control emulsion was 2.57%.

On the other hand, the same procedures as above were repeated, except that 5% of the gelatin in the emulsion was replaced by the styrene-maleic anhydride copolymer, to prepare an emulsion of the present invention. The gelatin concentration of this emulsion was 2.44%.

The two emulsions thus prepared were individually coated according to dipping method on a baryta paper having a basis weight of 190 g. so that the amount of each emulsion coated became 80 g./m.^{2}. The viscosities at 40° C. of the two emulsions and the coagulation temperatures thereof according to the PAGI method were as set forth in the following table:

Sample	Viscosity (40° C.), cp.	Coagulation temperature, ° C.
Control emulsion	2.9	18.0
Present emulsion	9.5	22.0

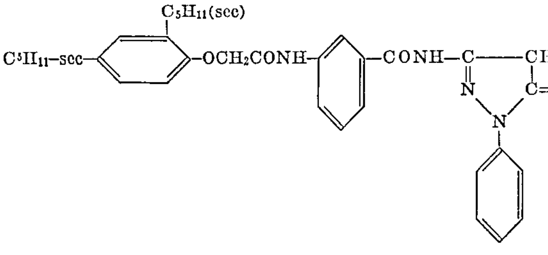
When subjected to coating, the control emulsion flowed even though the coating was effected in cold air at 10° C., whereas the present emulsion sufficiently set at a rate of 2.5 m./min. and did not flow at all.

EXAMPLE 5

Polyvinyl alcohol (polymerization degree 500)	g	50
Styrene-maleic anhydride copolymer	g	50
Water	ml	700

The above-mentioned components were dissolved together at an elevated temperature, and the resulting solution was adjusted to pH 4.0 and heated with stirring at

97° C. for about 4 to 6 hours. After cooling the solution to room temperature, the total amount was made 800 g. and the pH was controlled to prepare a dope convenient for use.



(1

3 g. of a magenta coupler of the above Formula 1 was dissolved in a mixture comprising 5 g. of tricresyl phosphate and 10 g. of ethyl acetate, and the resulting solution was dispersed by means of a homogenizer in 100 ml. of 5% gelatin containing 0.3 g. of saponin. The dispersion was added to a gelatin chlorobromide emulsion containing 5 g. of silver halide. Subsequently, the emulsion was charged with additives, and then the total amount thereof was made 640 g. to prepare a control emulsion. The total amount of gelatin contained in the control emulsion was 25.6 g.

On the other hand, an emulsion of the present invention was prepared in the same manner as above, except that 28 g. of the aforesaid dope of the condensation reaction product of styrene-maleic anhydride copolymer and polyvinyl alcohol was used to reduce the amount of gelatine.

The two emulsions thus prepared were individually coated according to dipping method on a baryta paper having a basis weight of 210 g. The emulsions were so coated that the amounts of the coupler coated became identical.

	Gelatin, percent	Viscosity at 40° C., cp.	Coagulation temperature, ° C.	Amount of coated ploymer, g./m.²
Control emulsion	4.0	4.9	19.5	3.2
Present emulsion	1.7	20.5	23.0	2.0

The two emulsions were set and coated without flowing, but the present emulsion could make the film thickness about 40% thinner than in the case of the control emulsion. After drying, the resulting photographic materials were individually exposed through an optical wedge, developed by use of a color developer of the composition shown below, and then subjected to ordinary fixing, water-washing, bleaching, water-washing, hardening-fixing and water-washing treatments.

COLOR DEVELOPER

N,N-diethyl-p-aminoaniline sulfate	g.	3.0
Sodium sulfite	g.	2.0
Sodium carbonate (monohydrate)	g.	300.0
Caustic soda	g.	1.0
Hydroxylamine sulfate	g.	2.0
Potassium bromide	g.	1.0
Benzyl alcohol	ml.	5.0

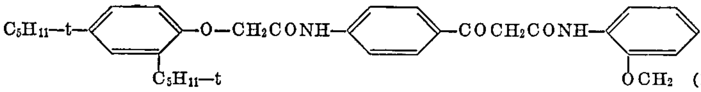
Water to make 1,000 ml.

The photographic properties of the individual photographic materials were as shown in the table below, and, as is clear from the table, the emulsion of the present invention was more increased in speed.

	Relative speed	Fog
Control emulsion	100	0.04
Present emulsion	130	0.04

Thus, according to the present invention, not only has it been made possible that an emulsion containing an oil-soluble coupler which tends to flow at the time of coating is successfully coated in the form of a gelatin solution extremely low in concentration, but also a multi-layered color photographic material excellent in developability can be provided since the coating film can be made thin.

EXAMPLE 6



(1)

10 g. of a yellow coupler of the above Formula 1 was dispersed in gelatine according to an ordinary procedure. The resulting dispersion was added to a silver iodobromide emulsion containing 10 g. of silver halide, and the total amount was made 540 g. to prepare a control emulsion.

On the other hand, an emulsion of the present invention was prepared in the same manner as above, except that 8% of the gelatin in the yellow emulsion was substituted by the copolymer of Example 2.

The thus prepared two emulsions were measured in minimum gelatin concentrations at the time when the amounts of coated coupler and silver halide became identical and when the coated state of the emulsions was favorable. Further, the amounts of adhered polymer at that time were also measured. The results were as set forth in the following table:

	Total amount of emulsion, g.	Gelatin, percent	Amount of coated emulsion, g./m.²	Amount of adhered polymer, g./m.²
Control emulsion	540	4.32	70	3.02
Present emulsion	540	1.89	70	1.56

Thus, in the case of the present emulsion, the film was about 50% thinner than in the case of the control emulsion. The photographic properties obtained through the same color development treatment as in Example 5 were as shown in the following table:

	Relative speed	Fog
Control emulsion	100	0.01
Present emulsion	140	0.02

As shown in the above examples, there has been developed a process in which a color photographic emulsion containing an oil-soluble coupler which is in the form of a gelatin solution can be thinly coated on a support without flowing.

What is claimed is:

1. In a photographic silver halide emulsion having dispersed therein an oil-soluble coupler, said silver halide emulsion containing gelatin, the improvement in which said silver halide emulsion contains a condensation reaction product of a styrene/maleic anhydride copolymer and polyvinyl alcohol.

2. The silver halide emulsion according to claim 1, wherein the blending ratio of said styrene/maleic anhydride copolymer to polyvinyl alcohol is 1:0.5 to 1:4 in the preparation of said condensation reaction product.

3. The silver halide emulsion according to claim 1,

wherein the polymerization degree of said polyvinyl alcohol is 500 to 1,000.

4. The silver halide emulsion according to claim **1**, wherein said condensation reaction product is present in an amount of 2 to 40% based on the gelatin.

5. The silver halide emulsion according to claim **1**, wherein said emulsion further contains a styrene/maleic anhydride copolymer such that said styrene/maleic anhydride copolymer and said condensation reaction product of said copolymer and polyvinyl alcohol are present in an amount of 2–40%, based on said gelatin.

6. The silver halide emulsion according to claim **1**, wherein said condensation product is present in an amount of 5 to 15% based on said gelatin.

7. A layer of a color photographic material which comprises a silver halide emulsion having dispersed therein an oil-soluble coupler, said silver halide emulsion containing gelatin and a condensation reaction product of styrene/maleic anhydride copolymer and polyvinyl alcohol.

8. The layer of a color photographic material according to claim **7**, wherein the ratio of said copolymer to polyvinyl alcohol is 1:0.5 to 1:4 in the preparation of said condensation reaction product.

9. The layer of a color photographic material according to claim **7**, wherein said condensation reaction product is present in an amount of 2–40% based on the gelatin.

10. The layer of a color photographic material according to claim **7**, wherein the polymerization degree of said polyvinyl alcohol is 500 to 1,000.

11. The layer of a color photographic material according to claim **7**, wherein said condensation reaction product is present in an amount of 5–15% based on said gelatin.

12. The layer of a color photographic material according to claim **7**, wherein said emulsion further contains a styrene/maleic anhydride copolymer such that said styrene/maleic anhydride copolymer and said condensation reaction product of said copolymer and polyvinyl alcohol are present in an amount of 2 to 40% based on the gelatin.

13. A multilayered color photographic material comprising at least one layer of a silver halide emulsion having an oil-soluble coupler dispersed therein, said silver halide emulsion containing gelatin and a condensation reaction product of styrene/maleic anhydride copolymer and polyvinyl alcohol.

14. The multilayered color photographic material according to claim **13**, wherein said condensation reaction product is present in an amount of 2–40% based on the gelatin.

15. The multilayered color photographic material according to claim **13** wherein the polymerization degree of said polyvinyl alcohol is 500 to 1,000.

16. The multilayered color photographic material according to claim **13**, wherein the ratio of said copolymer to polyvinyl alcohol is in the range of 1:0.5 to 1:4 in the preparation of said condensation reaction product.

17. The multilayered color photographic material according to claim **13**, wherein said condensation reaction product is 5–15% based on the amount of the gelatin of the emulsion.

18. The multilayered color photographic material according to claim **13**, wherein each layer comprises a silver halide emulsion having dispersed therein an oil-soluble coupler, said silver halide emulsion containing gelatin and a condensation reaction product of styrene/maleic anhydride copolymer.

19. The multilayered color photographic material according to claim **18**, wherein said condensation reaction product is present in an amount of 2–40% based on the gelatin.

20. The multilayered color photographic material according to claim **18**, wherein said emulsion further contains a styrene/maleic anhydride copolymer such that said styrene/maleic anhydride copolymer and said condensation reaction product of said copolymer and polyvinyl alcohol are present in an amount of 2 to 40% based on the gelatin.

21. The multilayered color photographic material according to claim **20**, wherein the polymerization degree of said polyvinyl alcohol is 500 to 1,000.

22. The multilayered color photographic material according to claim **18**, wherein the polymerization degree of said polyvinyl alcohol is 500 to 1,000.

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CERTIFICATE OF CORRECTION

Patent No. U.S. 3,723,127 Dated March 27, 1973

Inventor(s) Tetsuo YANO, Noboru ITOH, Sigeru IGUCHI, Bunzo UEDA, and Eiji KANADA

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In Column 1, line 6, the word "Inc." should read --Ltd.--

Signed and sealed this 13th of November 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents