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PHOTOGRAPHIC PRINTING ELEMENT CONTAINING FLUORESCENT DYE

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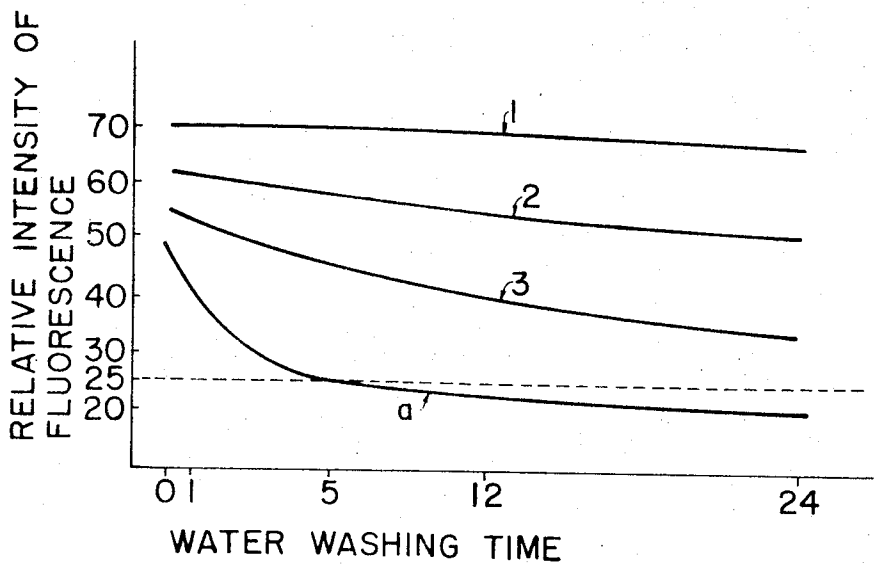

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PHOTOGRAPHIC PRINTING ELEMENT CONTAINING FLUORESCENT DYE

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Int. Cl. G03c 1/92
U.S. Cl. 96—82 9 Claims

ABSTRACT OF THE DISCLOSURE

A photographic printing element containing a water-soluble fluorescent whitening dye and a water-soluble polymer of an N-vinylamide compound.

The present invention relates to a photographic printing element and in particular to a photographic printing element having improved whiteness in the absence of a matt surface.

Hitherto, in order to improve the whiteness of non-image (blank) portions of a printed photographic printing element, it has been attempted to incorporate a fluorescent whitening dye, which emits a purple or a blue fluorescence by absorbing ultraviolet rays, in photographic layers, such as a baryta layer, an undercoating, a light-sensitive emulsion layer, a protective layer applied to a support or an image receiving layer of a printing element for diffusion transfer photography (hereinafter, these layers are called "photographic layers"). Water-soluble polyvinyl pyrrolidone in one of these photographic layers, and water-soluble poly-N-vinyl-5-methyl-2-oxazolidinone have also been incorporated in one of these layers for this purpose.

However, the conventional method of incorporating a fluorescent whitening dye has the drawback that, since the fluorescent whitening dye is not absorbed on the colloidal component of photographic layers, such as gelatin, although the fluorescent dye has a direct dyeing affinity to fibers, the intensity of fluorescence emitted from the fluorescent whitening agent incorporated in photographic layers is weaker than the case where the same fluorescent dye is absorbed on fibers, and sufficient whitening effect is not obtained. Furthermore, the greater part of the fluorescent whitening dye present in the photographic layer is removed in the water-washing stage after development, which severely weakens the whitening effect.

The aforesaid method of incorporating water-soluble poly-N-vinyl-5-methyl-2-oxazolidine or water-soluble polyvinyl pyrrolidone in the photographic layer has the drawback that, although the whitening effect is higher as the degree of polymerization of the polymer to be employed is higher, when a polymer having a high degree of polymerization is employed, the surface of the photographic printing element is matted.

Therefore, an object of the present invention is to provide a photographic printing element having improved whiteness by employing a water-soluble fluorescent whitening dye without the accompaniment of the aforesaid drawbacks.

Another object of the present invention is to provide a water-soluble high molecular weight compound to be employed together with a fluorescent whitening dye for improving the whiteness of a photographic printing element by being incorporated in a photographic layer of the element without being accompanied by the aforesaid drawbacks.

We have found that the above objects can be achieved by the incorporation of a fluorescent whitening dye and a water-soluble high molecular weight compound, which compound is prepared by polymerizing an N-vinylamide compound represented by the formula

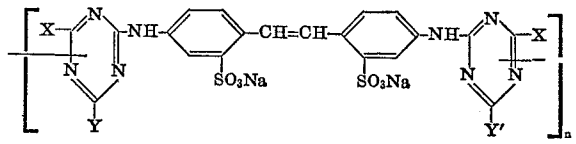
$$CH_2=CHNR_1COR_2$$

wherein R_1 represents methyl or ethyl and R_2 represents hydrogen, methyl or ethyl, or copolymerizing the above monomer with another comonomer, in at least one of the photographic layers of a photographic printing element, such as, a baryta layer, an undercoating, a light-sensitive emulsion layer, a protective layer, or a diffusion transfer image-receiving layer applied on a support.

The water-soluble fluorescent whitening dye (or fluorescent brightening agent) to be employed in the present invention is one which emits a blue-purple fluorescence (of wave lengths of 430–470 mu.) by absorbing ultraviolet rays. As fluorescent whitening dyes which may be employed in the present invention, there may be mentioned those known water-soluble fluorescent dyes having a direct dyeing affinity, such as diaminostilbene dyes, benzidine dyes, triazole dyes, imidazole dyes, and imidazolone dyes. Specific examples of such fluorescent whitening dyes are as follows:

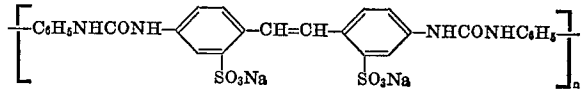
Diaminostilbene fluorescent dyes

(a) Compounds of the formula



(1)

wherein X, Y, X', and Y' each represents $-NHC_6H_5$, $-NHC_6H_4SO_3Na$, $-OH$, $-NH_2$, $-NHCH_2CH_2SO_3Na$, $-OCH_2CH_2OH$, or $-OCH_3$ and *n* represents 5 to 100.

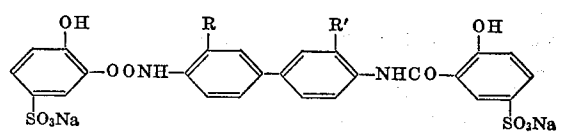


(b) (2)

wherein *n* represents 5 to 100.

Benzidine fluorescent dyes

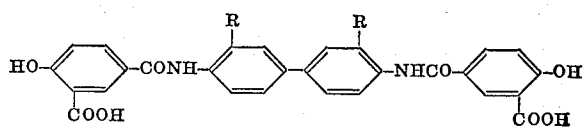
(a) Compounds of the formula



(3)

wherein R and R' each represents H, $-CH_3$ or $-OCH_3$.

(b) Compounds of the formula

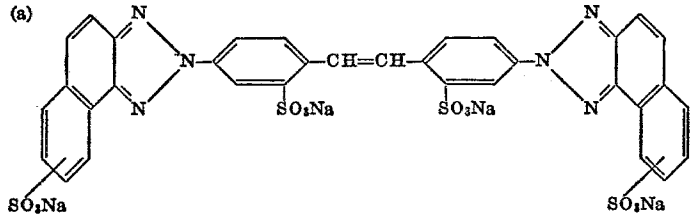


(4)

wherein R represents H, $-CH_3$, $-OCH_3$.

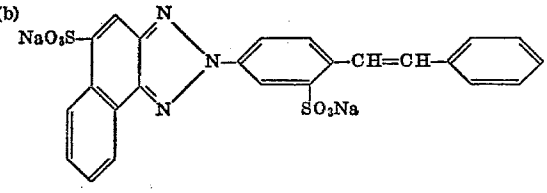
Triazole fluorescent dyes

(a)



(5)

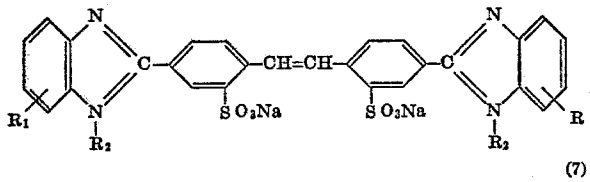
(b)



(6)

Imidazole fluorescent dyes

Compounds of the formula

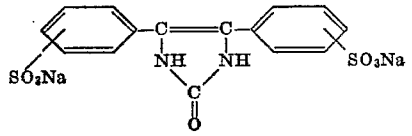


(7)

wherein R_1 represents —H, —CH_3, —C_2H_5, —OCH_3, or —SO_3Na and R_2 represents —H, —CH_3 or

—CH_2CH_2OH

Imidazolone fluorescent dye

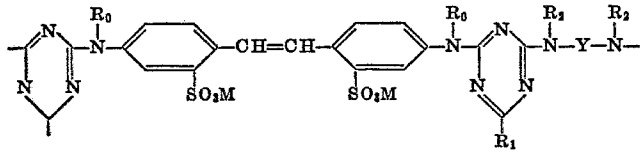


(8)

The above dye is disclosed in applicants' Japanese patent application No. 22,756/67.

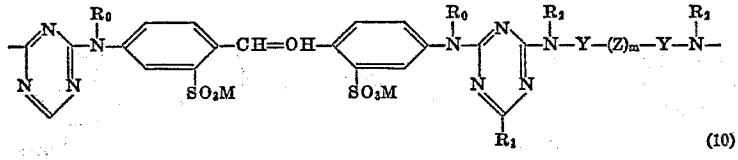
High molecular weight compounds having at least one of the repeating units represented by general Formulas (9) and (10)

Compounds of the formula



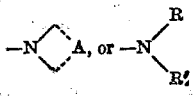
(9)

or



(10)

wherein R_0 and R_2 each represents a hydrogen atom, an alkyl group having 1–8 carbon atoms, an aryl group having 6–12 carbon atoms, a hydroxyalkyl group having 2–4 carbon atoms, a substituted hydroxyalkyl group, a sulfoalkyl group having 1–4 carbon atoms, an alkali metal salt thereof, or an ammonium salt; R_1 represents a halogen atom, —CR, —SR,



R and R′ each represents a hydrogen atom, an alkyl or hydroxyalkyl group having 1–12 carbon atoms, a sulfoalkyl group (or an alkali metal salt or ammonium salt thereof), a carboalkyl group (or an alkali metal or ammonium salt thereof), an aralkyl group, an aryl group having 6–18 carbon atoms, a hydroxycarboxy or sulfonic acid derivative of the aryl group, or an alkali metal or ammonium salt of the aryl group, a cycloalkyl group having 6–10 carbon atoms, or a substituted cycloalkyl group; A represents an alkylene group having 4–5 carbon atoms or an alkylene group having a hetero atom or hetero atomic group; Y represents an alkylene group having 2–10 carbon atoms, a substituted alkylene group, an alkylene group having 6–18 carbon atoms, or a substituted alkylene group; Z represents a divalent hetero atom or atomic group; m is 0 or 1; and M represents an alkali metal or ammonium group.

These fluorescent whitening dyes which may be employed in the present invention are well-known to those skilled in the art and are readily commercially available by the trade names of "Blankophor" (Farbenfabriken Bayer A. G.), "Leucophor" (Geigy Chemical Corp.), "Tinopal" (Sandoz A. G.), "Uvitex" (Ciba Ltd.), "Kayaphor" (Nippon Kayaku K. K.), "Potamin White" (Dupont), "Whitex" (Sumitomo Chemical Industries Co.), and "YL" (Honshu Chemical Co.). For example, "Blankophor B" is a fluorescent whitening agent corresponding to Formula 1 and "Blankophor R" corresponds to Formula 2.

The water-soluble high molecular weight compound used in this invention may be either a homopolymer of an N-vinyl amide represented by the general formula

$$CH_2=CHNR_1COR_2$$

or a copolymer of such N-vinylamide and another monomer such as acrylamide, methacrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N,N-diethylacrylamide, acryloyl morpholine, N-methylolacrylamide, N-hydroxyethylacrylamide, acrylic acid, methacrylic acid, methyl acrylate, hydroxethyl acrylate, acrylonitrile, 1-vinyl-2-methylimidazole, N-vinylpyridine, 4-vinylpyridine, N-vinylpyrrolidone, N-vinyloxazolidinone, N-vinylcaprolactam, N-vinyl-5-methyl-2-oxazolidinone, vinyl acetate, maleic anhydride, sodium p-vinylbenzene sulfonate, or methyl vinyl ether.

The aforesaid N-vinylamide compound represented by the above general formula may be easily prepared by re-

acting the corresponding N-alkylacyl compound represented by the general formula R_2CONHR_1 and acetylene in an autoclave in the presence of an alkali catalyst.

As examples of the N-vinylamide compound, there may be mentioned N-vinyl-N-methylformamide (boiling point 73° C. at a pressure of 50 mm. Hg), N-vinyl-N-methyl acetamide (boiling point 63° C./17 mm. Hg), N-vinyl-N-methylpropionamide (boiling point 75° C./17 mm. Hg), N-vinyl-N-ethylformamide (boiling point 81° C./50 mm. Hg), and the like.

The desired polymer may be obtained by dissolving the above N-vinylamide compound in a solvent such as water, an alcohol, benzene, ligroin or the like and conducting the polymerization in a nitrogen gas stream at a temperature of about 40–100° C. in the presence of a catalyst such as hydrogen peroxide, potassium persulfate, 2,2'-azobis-butyronitrile, or the like.

In the case of preparing the copolymer of this invention, it is preferable for improving the whitening effect that the proportion of the aforesaid comonomer be less than 20 mole percent of the total amount of copolymer.

In order to obtain the desired whitening effect, higher molecular weight polymers are desirable for use in the present invention, and the molecular weight is preferably in the range of about 50,000–500,000 (intrinsic viscosity 0.2–1.5 in an aqueous solution at 30° C.). Particularly useful are polymers having a molecular weight of about 100,000–400,000 (intrinsic viscosity 0.5–1.2 in an aqueous solution at 30° C.). However, polymers possessing molecular weights above and below these ranges may be employed.

When using the aforesaid conventional N-vinylpyrrolidone polymer, if the molecular weight thereof is higher than 100,000, and particularly if it approaches about 360,000, the miscibility of the polymer with gelatin is degraded, whereby the surface of the photographic printing paper tends to be severely matted. On the other hand, the aforesaid N-vinylamide polymer of this invention having a molecular weight of higher than 100,000 shows a good miscibility with gelatin and moreover even if the molecular weight thereof is over 300,000, very little lack of miscibility occurs, provided the amount of the polymer employed is not excessive, that is, not more than about 60% by weight.

There exists no particular limitation on the amount of of the N-vinylamide polymer or copolymer of the present invention provided sufficient polymer is present to obtain the desired whitening effect. In general, at least 5% by weight of the polymer based upon the total weight of polymer and gelatin binder is desirable to obtain significant whitening effect. However, since the use of an excess amount of the polymer does not substantially increase the whitening effect over a value achieved by about 40% by weight, and in fact reduces miscibility with gelatin and causes a degradation of the quality of the image and is in addition uneconomical, the preferred amount of polymer employed is about 5–40% by weight. Most preferably, the amount employed is about 15–25% by weight.

As mentioned above, the photographic layers of the photographic printing element of this invention include any of a silver halide emulsion layer, a baryta layer, an undercoating, a protective layer applied to a support such as paper, synthetic resin film, a glass plate or a metal plate and an image receiving layer for a diffusion transfer printing element applied to the support. The fluorescent whitening dye and the water-soluble high molecular weight compound may be incorporated in any one of the above photographic layers to provide the desired effect. Further, the water-soluble high molecular weight material may be incorporated in a different photographic layer than the layer containing the fluorescent whitening dye.

Also, the invention has been exemplified above in terms of using gelatin as the binder. However, other binders such as synthetic resins may be similarly employed in the present invention.

By the present invention, a photographic printing element providing the same or a superior effect than conventional photographic elements containing an N-vinylpyrrolidone polymer or an N-vinyl-5-methyloxazolidione polymer is provided without resulting in the matting of the surface encountered in the conventional methods.

The invention will be explained more practically based on the following examples.

EXAMPLE I

To a gelatino silver halide emulsion containing 50 g. of gelatin and 20 g. of silver chlorobromide (containing 30 mole percent silver bromide) were added 0.5 g. of the fluorescent whitening agent "Blankophor BUP" (trade name of Farbenfabriken Bayer A. G.) and 10 g. of an N - vinyl - N - methylacetamide homopolymer having an intrinsic viscosity of 1.05, 0.58, or 0.32 in an aqueous solution of 30.0° C. Then, after adding to the emulsion formaldehyde as a hardening agent and saponin as a wetting agent, the resulting silver halide emulsion was applied to a photographic baryta paper of 150 g./sq. meter to provide a photographic paper. The photographic paper thus prepared was processed in a developer and a fixing solution having the following compositions respectively;

	G.
Developer:	
Metol (p-methylaminophenol sulfate)	1.0
Sodium sulfite (anhydrous)	15
Hydroquinone	4
Sodium carbonate mono-hydrate	27
Potassium bromide	1.3
Water to make, 1 liter.	
Fixing solution:	
Crystalline sodium thiosulfate	240
Sodium sulfite (anhydrous)	15
Glacial acetic acid	13.3
Borax	7.5
Powdered potassium alum	15
Water to make, 1 liter.	

The sample was washed with running water of 15° C. for 1, 5, or 24 hours.

The photographic paper thus prepared and processed was tested for intensity of fluorescence, the results of which are shown in the figure of the accompanying drawing. In the figure, there is shown the relation between the water-washing time and the relative intensity of fluorescence, which was a relative value when the whiteness of the surface of the photographic paper itself was assumed to be 25. In the figure, curve **1** stands for the results in the case of using the high molecular weight compound having an intrinsic viscosity of 1.05, curve **2** for the case of using the high molecular weight compound having an intrinsic viscosity of 0.58, and curve **3** for the case of using the high molecular weight compound of an intrinsic viscosity of 0.32. Curve (a) in the figure represents a control run, using a paper prepared as above, but having incorporated therein only the fluorescent whitening dye and not the water-soluble high molecular weight compound.

As will be understood from the results shown in the figure, the intensity of fluorescence of the photographic papers of this invention was remarkably higher than the result of the control sample shown by curve (a) and among the photographic papers of this invention, the sample having the water-soluble high molecular weight material having a higher molecular weight gave higher intensity of fluorescence. Moreover, even though the water-soluble high molecular weight compound having a higher molecular weight was employed, the surface properties of the photographic paper were not injured. Also, very little reduction in whiteness by water washing was observed.

EXAMPLE II

To one liter of a baryta coating dispersion having the following composition were added one gram of "Blanko-

phor BUP" as the fluorescent whitening dye and 10 g. of an N-vinyl-N-methylformamide polymer having an intrinsic viscosity of 1.05 (molecular weight of 40,000):

Barium sulfate	g.	500
Gelatin	g.	50
Chromium alum	g.	2
Formalin (30%)	ml.	0.3

Water to make, 1 liter.

The baryta coating composition was applied to a paper in a thickness of 100 g./sq. meter. To the baryta coated paper was applied a gelatino silver halide emulsion containing 50 g. of gelatin and 20 g. of silver chloride and having added thereto formaldehyde as a hardening agent and saponin as a wetting agent followed by drying.

The photographic paper thus prepared was processed as in Example I and the result was compared with a control paper wherein no N-vinyl-N-methylformamide polymer was incorporated in the baryta layer. The results showed that the whiteness of the surface of the photographic paper of this invention was much better than the control case. Moreover, the whitetness of the photographic paper of this invention was not reduced by water washing.

EXAMPLE III

After adding formaldehyde as a hardening agent and saponin as a wetting agent to a gelatino silver halide emulsion containing 20 g. of silver chlorobromide (60 mole percent silver bromide) per 50 g. of gelatin, the resulting silver halide emulsion was applied to a baryta coated paper of 150 g./sq. Before drying the silver halide emulsion layer, an aqueous solution containing 0.7 g. of "Whitex BF" (trade name of Sumitomo Chemical Industries Co.) as a fluorescent whitening dye, 8 g. of the N-vinyl-N-methylformamide having an intrinsic viscosity of 0.90, 3 ml. of formalin, 6 ml. of a 6% methanol solution of saponin, and one liter of water was applied to the silver halide emulsion layer in a setting state and dried. The photographic paper thus prepared was processed and dried as in Example I and the results were compared with a control paper having no N-vinyl-N-methylformamide polymer added. The results showed that the whiteness of the surface of the photographic paper of this invention was higher than the control case. Also, the whiteness of the photographic paper of this invention was not reduced by water washing.

EXAMPLE IV

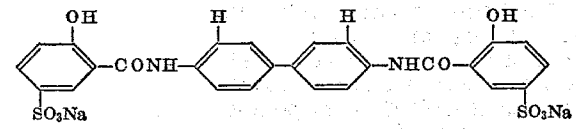
After adding 0.5 g. of "Kayaphor S" (trade name of Nippon Kayaku K. K.) as a fluorescent whitening agent and formaldehyde as a hardening agent and saponin as a wetting agent to a gelatino silver halide emulsion containing 20 g. of silver iodobromide (1.5 mole percent silver iodide) to 50 g. of gelatin, the resulting emulsion was applied to a baryta coated paper of 150 g./ sq. meter. To the silver halide emulsion layer in a setting state before drying was applied an aqueous solution containing 20 g. of gelatin, 8 g. of the N-vinyl-N-methylpropionamide polymer having an intrinsic viscosity of 0.98, 3 ml. of an aqueous 30% solution of formalin, 6 ml. of a 6% methanol solution of saponin, and one liter of water followed by drying to provide a protective layer.

The photographic paper thus prepared was processed and dried as in Example I and the results were compared with a control having no added N-vinyl-methylpropionamide polymer in the protective layer. The results showed that the whiteness of the surface of the photographic paper of the present invention was much better than in the control. Moreover, the whiteness was not reduced by water washing after processing.

EXAMPLE V

To the baryta coating composition as shown in Example II was added 12 g. of an N-vinyl-N-methylformamide polymer having an intrinsic viscosity of 0.85 and

the resulting composition was applied to a paper of 100 g./sq. meter followed by drying. To the baryta layer was applied a gelatino silver halide emulsion containing 20 g. of silver chlorobromide (30 mole percent silver bromide) to 50 g. of gelatin and having added thereto formaldehyde as a hardening agent and saponin as a wetting agent. Further, to the silver halide emulsion layer in a setting state before drying was applied an aqueous solution containing 20 g. of gelatin, 1 g. of the benzidine fluorescent whitening dye of the formula

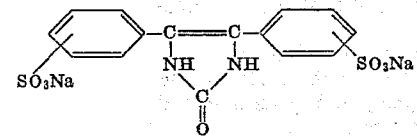


3 ml. of an aqueous 30% solution of formalin, 6 mil of a 6% alcohol solution of saponin, and one liter of water followed by drying.

The photographic paper thus prepared was processed and dried as in Example I and the results were compared with a control having no added N-vinyl-N-methylformamide polymer. The whiteness of the photographic paper of this invention was much better than the control and also was not reduced by water washing after processing.

EXAMPLE VI

After adding to one liter of the baryta coating composition as shown in Example II one gram of the imidazolone fluorescent whitening dye represented by the formula



as the fluorescent whitening agent, the resulting composition was applied to a paper of 100 g./sq. meter followed by drying. Thereafter, a gelatino silver halide emulsion containing 20 g. of silver iodobromide (1.5 mole percent silver iodide) to 50 g. of gelatin having added thereto 12 g. of a copolymer having a mole ratio of N-vinyl-N-methylacetamide to acrylamide of 9:1 and an intrinsic viscosity of 0.85, formaldehyde as a hardening agent, and saponin as a wetting agent was applied to the baryta layer followed by drying.

The photographic paper thus prepared was processed and dried as in Example 1 and the results were compared with a control wherein the aforesaid copolymer was not incorporated in the emulsion layer. The results showed that the whiteness of the surface of the photographic paper of this invention was much better than the control case and was not reduced by water washing after processing.

EXAMPLE VII

To one liter of a aqueous 5% gelatin solution containing colloidal nickel sulfite were aded 0.5 g. of "Tinopal GS" (trade name of Sandoz A. G.) as a fluorescent whitening dye and 12 g. of a copolymer having a mole ratio of N-vinyl-N-methylformamide to methacrylamide of 9:1 and an intrinsic viscosity of 0.75 and the resulting solution was applied to a paper of 85 g./sq. meter. On the layer thus formed was applied a stripping layer mainly consisting of sodium alginate to provide a diffusion transfer image receiving element.

The image receiving element thus prepared was closely placed on a light-sensitive layer having a silver halide emulsion layer which had been exposed. The assembly was passed through a diffusion transferring device and a developer and the image receiving element was stripped from the light-sensitive element after 30 seconds. The results were compared with a control wherein the aforesaid copolymer was not employed. The results showed that the whiteness of the white background portions of the positive image was better than the control.

EXAMPLE VIII

To a gelatino silver halide emulsion containing 20 g. of silver chlorobromide (30 mole percent silver bormide) to 50 g. of gelatin was added 10 g. of an N-vinyl-N-methylacetamide polymer having an intrinsic viscosity of 1.05 and the resulting silver halide emulsion was, after the addition of formaldehyde as a hardening agent and saponin as a wetting agent, applied to a baryta coated paper of 150 g./sq. meter. The photographic layer was developed in the developer of Example I, but having added thereto 0.7 g./liter of "Blankophor BUP" and then fixed, washed with water and dried as in Example I. The results were compared with a control where no N-vinyl-methylacetamide polymer was added to the silver halide emulsion layer. The whiteness of the surface of the photographic paper of this invention was better than the control and was not reduced by water after processing.

What is claimed is:

1. A photographic printing element having photographic layers, at least one of said photographic layers containing a water-soluble fluorescent whitening dye and a water-soluble member selected from the group consisting of a polymer and a copolymer of a compound represented by the formula

wherein R_1 represents a radical selected from the group consisting of methyl and ethyl and R_2 represents a radical selected from the group consisting of hydrogen, methyl and ethyl.

2. The photographic printing element as claimed in claim 1 wherein said water-soluble fluorescent whitening dye is selected from the group consisting of a diaminostilbene fluorescent dye, a benzidine fluorescent dye, a triazole fluorescent dye, an imidazole fluorescent dye and an imidazolone fluorescent dye.

3. The photographic printing element as claimed in claim 1 wherein said compound is selected from the group consisting of N-vinyl-N-methylformamide, N-vinyl-N-methylacetamide, N-vinyl-N-methylpropionamide, and N vinyl-N-ethylformamide.

4. The photographic printing element as claimed in claim 1 wherein said photographic layer is selected from the group consisting of a baryta layer, an undercoating layer, a light-sensitive silver halide emulsion layer and a protective layer.

5. The photographic printing element as claimed in claim 1 wherein said photographic layer is a diffusion transfer image receiving layer.

6. A photographic printing element as claimed in claim 1 wherein said member is a homopolymer.

7. A photographic printing element as claimed in claim 1 wherein said member is a copolymer of said compound and another vinyl monomer.

8. A photographic printing element as claimed in claim 1 wherein the water-soluble fluorescent dye and the water-soluble member selected from said group are in different photographic layers of said element.

9. A photographic printing element as claimed in claim 1 wherein said water-soluble member has a molecular weight of about 50,000–500,000.

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RONALD H. SMITH, Primary Examiner

U.S. Cl. X.R.

96—85, 87 R, 76 R, 114; 117—33.5 T