

1

2

3,677,762

COLOR ELEMENTS CONTAINING BRIGHTENING AGENTS AND ULTRAVIOLET ABSORBERS

Hiroyuki Amano, Nobuo Tsuji, and Kazuo Shirasu, Minami-Ashigara-machi, Kanagawa, Japan, assignors to Fuji Photo Film Co., Ltd., Minami-Ashigara-machi, Kanagawa, Japan

No Drawing. Filed Jan. 8, 1970, Ser. No. 1,564

Claims priority, application Japan, Jan. 8, 1969, 44/1,554

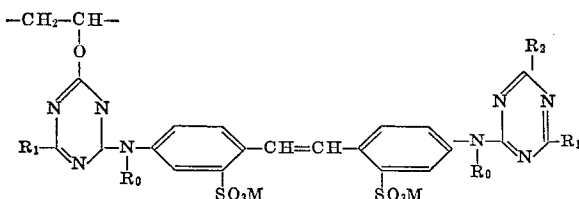
Int. Cl. G03c 1/76

U.S. Cl. 96-74

12 Claims

ABSTRACT OF THE DISCLOSURE

Color printing papers comprising multiple photographic layers, wherein at least one of the layers contains an ultraviolet absorber, with one of the layers containing a fluorescent brightening agent having the repeating formula



are disclosed. The color printing papers have increased whiteness.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The present invention relates to a color printing paper containing a fluorescent brightening agent and an ultraviolet absorber and more particularly to a color printing paper which has been fluorescent-brightened by incorporating a ballasting or diffusion resistant and water soluble fluorescent brightening agent and which is prevented from being faded and stained by the action of ultraviolet rays due to the incorporation in the printing paper of an ultraviolet absorber.

(2) Description of the prior art

Incorporation of a fluorescent brightening agent in the baryta coating of a baryta coated printing paper generally has been the means for improving the whiteness of printing papers. However, where this method has been used with color printing paper for improving baryta-coated paper, the brightening effect of the fluorescent brightening agent is minimal since compounds, such as ultraviolet absorbers and couplers, absorbing in the ultraviolet regions are incorporated in the photographic layers applied to the baryta coating containing the fluorescent brightening agent.

To improve the brightening effect of the fluorescent brightening agent much work has been done. For instance, a method of dyeing a protective colloid, gelatin, with a fluorescent brightening agent by treating the gelatin with a solution of a water-soluble fluorescent brightening agent is known. However, with this method, it is difficult to dye selectively the desired photographic layer with a fluorescent brightening agent. In addition, the method is inconvenient in that an additional fluorescent brightening bath is required.

Other methods are known. A direct addition method, in which a solution of a fluorescent brightening agent in water or an organic solvent is directly incorporated into a photographic emulsion layer or a subsidiary layer, and

an indirect addition method, in which a solution of a fluorescent brightening agent in a high boiling solvent or a mixture of a high boiling solvent and an auxiliary solvent are emulsified in an aqueous gelatin solution and the emulsion is incorporated in a photographic emulsion layer or a subsidiary layer, are known. However, since known fluorescent brightening agents are generally low molecular weight compounds, a large proportion of the compound is dissolved off in photographic processing or washing, even where the fluorescent brightening agent is incorporated in a photographic emulsion layer of a subsidiary layer as mentioned above. This results in a reduction in the brightening effect.

Development work directed to these problems has been undertaken to overcome these difficulties. For example, a method is known in which a substituent for improving the dyeing affinity of gelatin is introduced into the gelatin. Subsequently the gelatin is dyed with a fluorescent brightening agent. A method is also known in which a compound having a good dyeing affinity for a fluorescent brightening agent, such as polyvinylpyrrolidone (see Japanese patent publication 7,127/59) or poly-N-vinyl-5-methyl-2-oxazolidinone (see Japanese patent publication 22,065/64), is dispersed in an aqueous gelatin solution and then the gelatin is dyed with the fluorescent brightening agent. With such known methods loss of the fluorescent brightening agent still occurs and hence the brightening effect is reduced considerably due to photographic processing and washing.

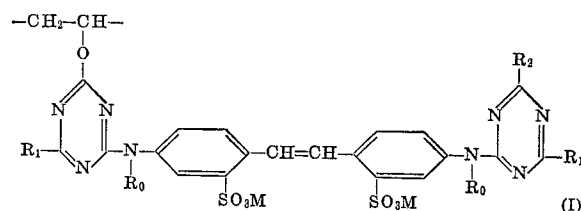
It is also known to incorporate an ultraviolet absorber in a layer on an emulsion layer or in the emulsion layer to improve the light fastness of a color image formed on the emulsion layer. Ultraviolet absorbers usually employed for this purpose mainly absorb ultraviolet rays in the range of from 300 to 400 m. It is also known that use of ultraviolet absorbers absorbing ultraviolet rays of wavelengths as long as possible is effective. However, if the absorption of the ultraviolet absorber extends to wavelengths over 400 m, the compound is yellow in color and has an adverse effect on the whiteness of background. Therefore, it is desirable to apply a fluorescent brightening agent-containing layer on an ultraviolet absorber containing layer to prevent coloring by the ultraviolet absorber and also to complement the reduced brightening effect by the incorporation of an ultraviolet absorber as mentioned above.

An object of the present invention is to provide a color photographic printing paper having a sufficient whiteness and for which fading is minimized by the presence of an ultraviolet absorber. That is, the object of the present invention is to provide a color photographic printing paper in which an ultraviolet absorber and a fluorescent brightening agent are employed in which the functions of both can be obtained.

DESCRIPTION OF THE INVENTION

The object of the present invention is achieved according to the invention described herein.

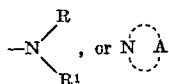
It has been found that when a high molecular weight compound having the repeating unit represented by the general formula (I):



wherein R₀ represents a hydrogen atom, an alkyl group

3

having from 1 to 8 carbon atoms, an aryl group having from 6 to 12 carbon atoms, a hydroxyalkyl group having from 2 to 4 carbon atoms, a derivative of said hydroxyalkyl group, a sulfoalkyl group having from 1 to 4 carbon atoms, or an alkali metal or ammonium salt of said sulfoalkyl group; R_1 and R_2 each represents a halogen atom, —OR, —SR,



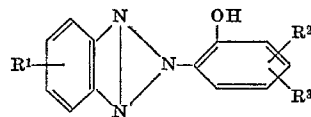
R and R' represents a hydrogen atom, an alkyl group having from 1 to 12 carbon atoms, a hydroxyalkyl group, a sulfoalkyl group, an alkali metal or an ammonium salt of said sulfoalkyl group, a carboxyalkyl group, an alkali metal or an ammonium salt of said carboxyalkyl group, an aralkyl group, an aryl group having from 6 to 18 carbon atoms, a substituted aryl group by a substituent such as a hydroxy group, a carboxyl group, or a sulfonic acid group, an alkali metal or an ammonium salt of said sulfonic acid group, a cycloalkyl group having from 6 to 10 carbon atoms, or a substituted cycloalkyl group; A represents an alkylene group having from 4 to 5 carbon atoms or an alkylene group containing a hetero-atom or a hetero-atomic group; and M represents an alkali metal atom or ammonium group, is incorporated in a photographic layer containing the ultraviolet absorber or in at least a layer provided on the photographic layer containing the ultraviolet absorbent the above-mentioned drawbacks can be minimized. That is, the high molecular weight compound mentioned above is dissolved off in the steps of photographic processing and washing to a lesser extent, does not stain when the compound is decomposed by ultraviolet rays, and also has excellent fluorescent strength and wave length.

As an example of a color photographic printing paper, a baryta-containing layer, a blue-sensitive emulsion layer containing a yellow coupler, an intermediate layer, a green-sensitive emulsion layer containing a magenta coupler, an intermediate layer, a red-sensitive emulsion layer containing a cyan coupler, and a protective layer are formed on a support paper in this order. In this example, an ultraviolet absorber is usually incorporated in an intermediate layer between the cyan coupler-containing emulsion layer and the magenta coupler-containing emulsion layer and a fluorescent brightening agent is incorporated in the protective layer.

Examples of suitable ultraviolet absorbers used in the

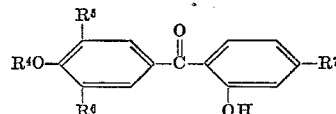
4

present invention are benztriazole derivatives represented by the general Formula II



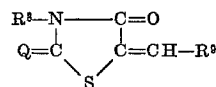
(II)

wherein R^1 , R^2 , and R^3 each represents a hydrogen atom, a halogen atom, a nitro group, an alkyl group, an aromatic ring, or a heterocyclic ring; benzophenone derivatives represented by the general Formula III



(III)

wherein R^5 and R^6 each represents an alkyl group and R^7 and R^4 each represents a hydrogen atom or an alkoxy group; thiazolidone derivatives represented by the general Formula IV



(IV)

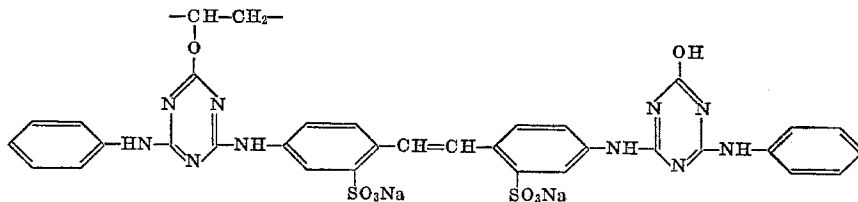
wherein R^8 represents a hydrogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, or an aryl group; R^9 represents an aryl group or a pyridyl group; and Q represents an imino group; cinnamic acid esters; oxazole derivatives; thiazole derivatives; imidazole derivatives; oxadiazole derivatives; thiadiazole derivatives; thiophenes; benzalazines; and bis-hydroxyaryl-amido compounds.

The aforesaid ultraviolet absorber can be dissolved in a high boiling solvent or in a mixture of a low boiling solvent and a high boiling solvent, the resulting solution is dispersed by emulsification in an aqueous gelatin solution, and the dispersion is added in the above-mentioned photographic layer or the ultraviolet absorbent can be added directly to the above-mentioned photographic layer, as a solution, as an alkaline aqueous solution.

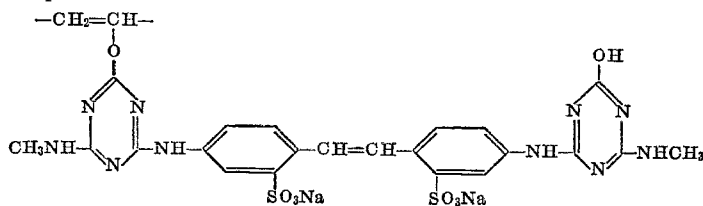
The high molecular weight fluorescent brightening agents used in the present invention and the methods of preparing them are described in detail in the specification of U.S. patent application Ser. No. 837,326, filed June 27, 1969, now U.S. Pat. 3,615,544.

Examples of these brightening agents are the high molecular weight fluorescent brightening agents having the following repeating units respectively:

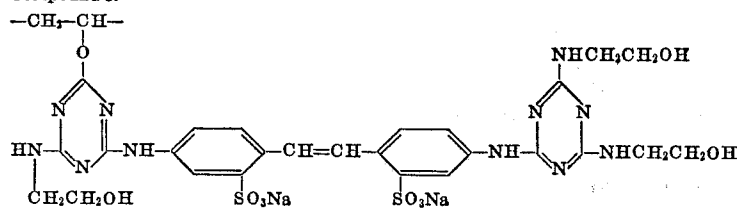
Compound 1;



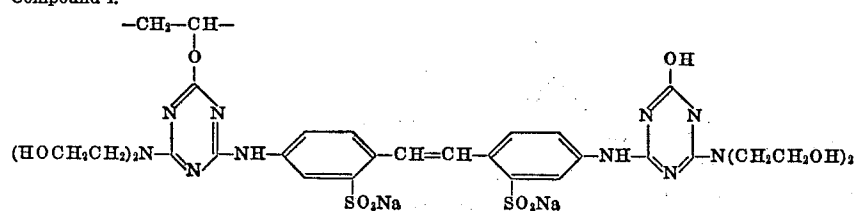
Compound 2:



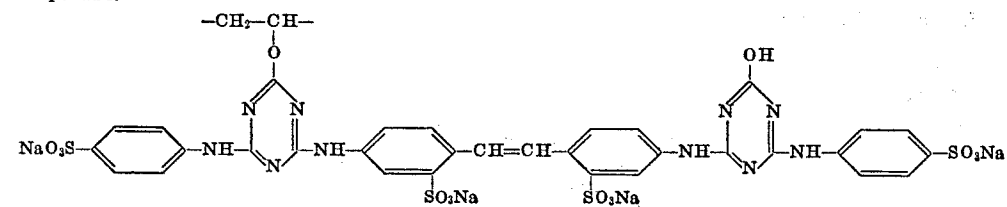
Compound 3:



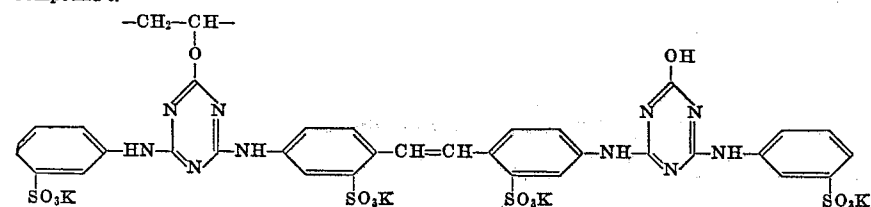
Compound 4:



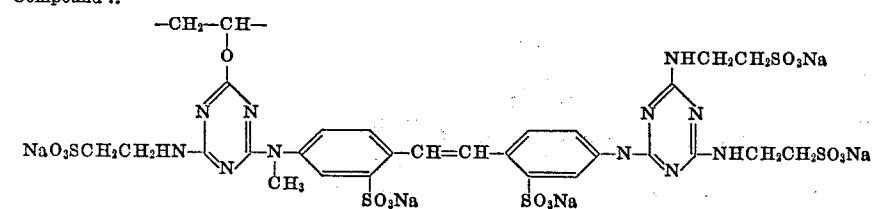
Compound 5:



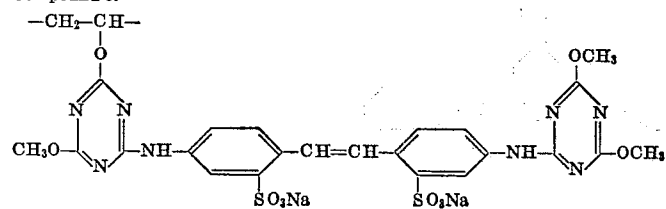
Compound 6:



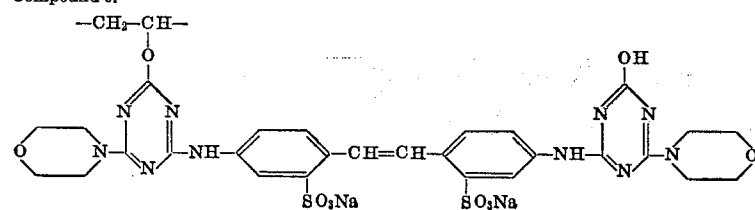
Compound 7:



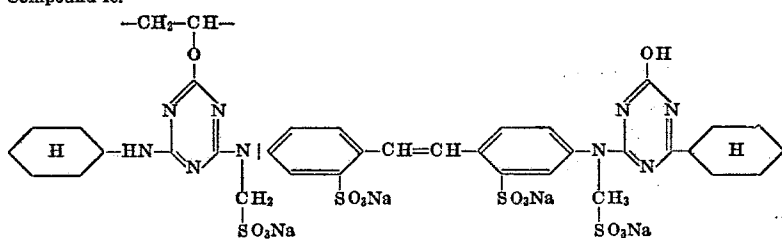
Compound 8:



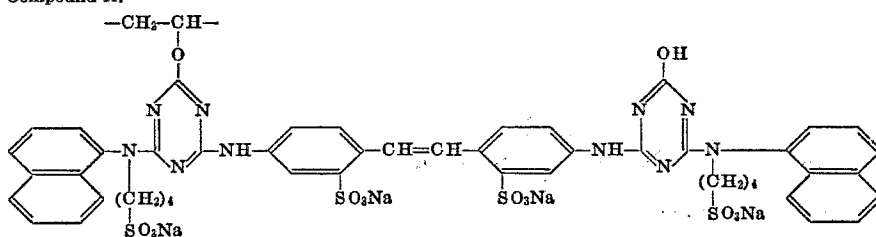
Compound 9:



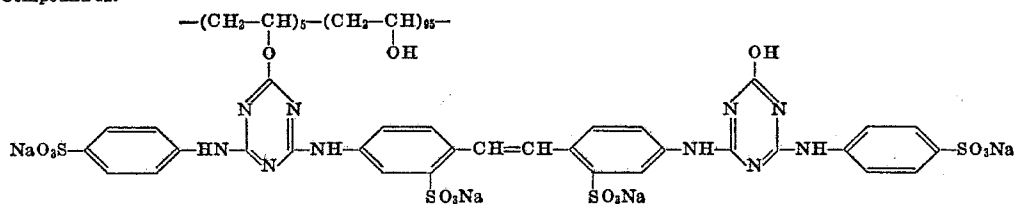
Compound 10:



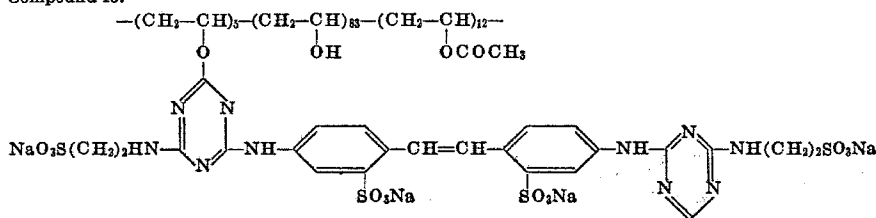
Compound 11:



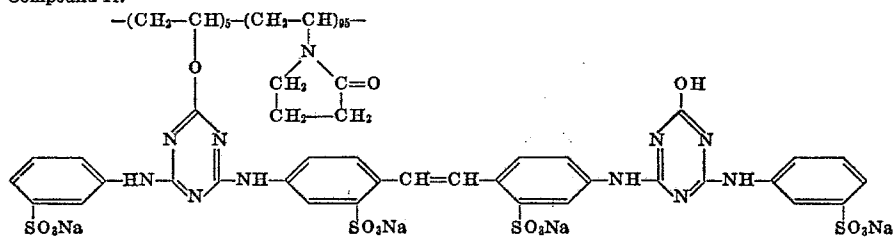
Compound 12:



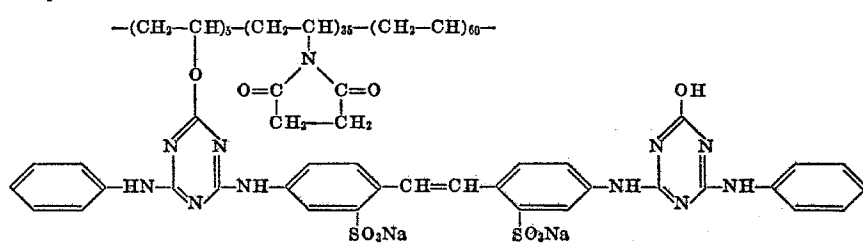
Compound 13:



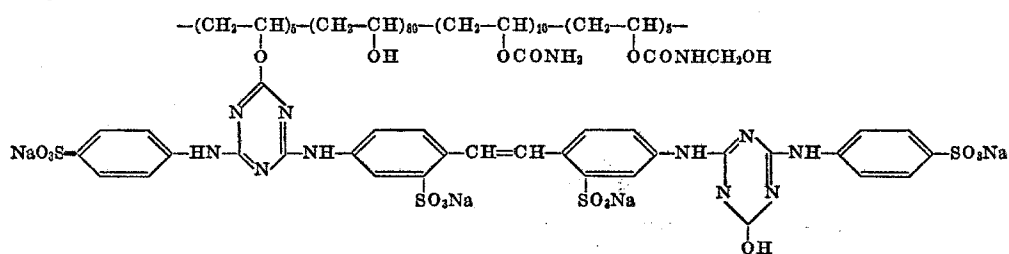
Compound 14:



Compound 15:



Compound 16:

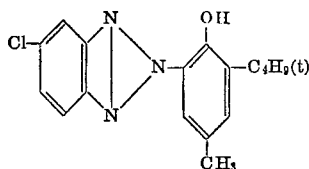


9

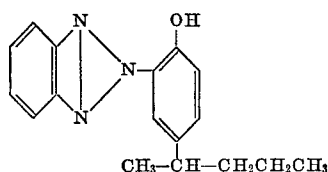
The high molecular weight fluorescent brightening agents suitable for use in the invention are polymeric materials and generally have molecular weights ranging from about 20,000 to 1,000,000. A range of from 100,000 to 400,000 is preferred.

Examples of the ultra-violet absorbers in the present invention are as follows. (t)=tertiary

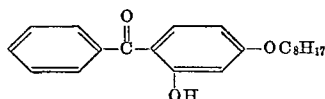
Compound 17:



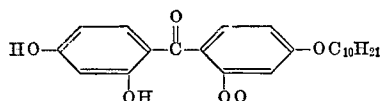
Compound 18:



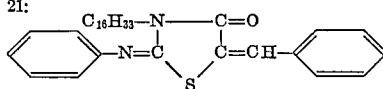
Compound 19:



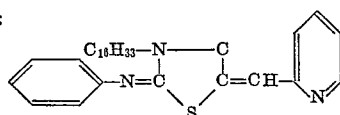
Compound 20:



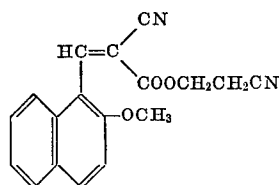
Compound 21:



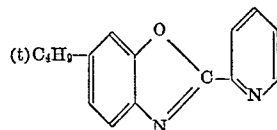
Compound 22:



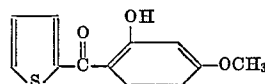
Compound 23:



Compound 24:



Compound 25:



The amount of the high molecular weight fluorescent brightening agent of the present invention to be incorporated in photographic layer is suitably from 0.5 to 10 mg./100 cm.² and that of the ultraviolet absorber is usually from 2 to 20 mg./100 cm.².

At the present time, almost all of the fluorescent brightening agents known at present also act simultaneously as ultraviolet absorbers. The high molecular weight fluorescent brightening agents used in the present inven-

10

tion also have ultraviolet absorbing functions. However, as mentioned above, the use of the fluorescent brightening agent results in insufficient ultraviolet absorbing effect. If the amount of the fluorescent brightening agent is increased to increase the ultraviolet absorbing effect, the density of the color image will be reduced and also the density of yellow component will be reduced.

Accordingly, in order to minimize sufficiently the occurrence of fading in and to provide sufficient whiteness to a color photographic printing paper, it is necessary to use an ultraviolet absorber and a fluorescent brightening agent simultaneously.

As mentioned above, the fluorescent brightening agent can be incorporated in the photographic layer by the indirect method or a direct method. When a conventional fluorescent brightening agent is incorporated in the uppermost photographic layer of a color photographic printing paper by the indirect addition method, the incorporated material is deposited by the application of mechanical impact or rubbing onto the printing paper, otherwise the printing paper becomes sticky or adheres to a sheet of an album on storage. Thus, when the conventional fluorescent brightening agent is employed, it cannot be incorporated in the uppermost layer. Conversely, the fluorescent brightening agent of the present invention can be incorporated in the uppermost layer without the aforesaid drawbacks. This makes it possible to utilize more effectively the function of the agent as fluorescent brightening agent.

Of course, when the high molecular compound of the present invention is incorporated in any other photographic layers than the uppermost layer, it also exhibits an ultraviolet absorbing effect and a fluorescent brightening effect.

The photographic silver halide emulsions employed in the color photographic printing paper of the present invention are usually gelatino silver halide light-sensitive emulsions. As the protective colloid for the emulsions, a synthetic resin such as polyvinyl alcohol or polyvinyl acetal can be employed in the present invention instead of gelatin.

An example of the layer construction of a color photographic printing paper is illustrated above. Color photographic printing papers having other layer constructions can be used in the present invention if desired. The ultraviolet absorber can be incorporated in any layer other than the protective layer, and the high molecular weight fluorescent brightening agent of the present invention can be incorporated in a layer containing the ultraviolet absorber or in a layer disposed on top of the layer containing the ultraviolet absorber, e.g., the layer containing the ultraviolet absorber lies closer to the support while the layer containing the fluorescent brightening agent lies farther from the support.

The following examples illustrate typical combinations of the water-soluble high-molecular weight fluorescent brightening agents of the present invention and the ultraviolet absorbers but the invention should not be interpreted as being limited to them. The brightening effect and ultraviolet preventing effect of the water-soluble high molecular weight fluorescent brightening agent itself of the present invention are described in the specification of copending U.S. patent application Ser. No. 837,326, now U.S. Pat. 3,615,544. The disclosure of this patent application is incorporated herein by reference.

EXAMPLE 1

Compound 14 shown above was incorporated in each layer of a color photographic printing paper and the effect thereof was investigated. In this example, two types of color photographic printing papers were used. Color photographic printing paper A was composed of a paper support having coated thereon a baryta-containing layer; a blue-sensitive emulsion layer containing a yellow coupler, 3,5 - dicarboxy-, -(4-stearoylamidobenzoyl)

acetanilide; an intermediate layer; a green-sensitive emulsion layer containing a magenta coupler, 1-(3-sulfo-4-phenoxyphenyl)-3-stearoyl-5-pyrazolone; an ultraviolet absorbing layer containing Compound 17, shown above; a red-sensitive emulsion layer containing a cyan coupler, N-n-octadecyl-1-hydroxy-4-sulfo-2-naphthamide; and a protective layer in this order. Color photographic printing paper B had the same layer construction except that the ultraviolet absorbing layer containing Compound 17 was replaced with an intermediate gelatin layer containing no ultraviolet absorber. In these color printing papers, the fluorescent brightening agent of the present invention, Compound 14, was incorporated in each of the seven photographic layers in an amount of 5 mg./100 cm.² to prepare seven different color printing papers. These color photographic printing papers were subjected to conventional color photographic processing and the whiteness of the printing papers thus processed was measured. The results obtained are shown in the following table. The whiteness in the table is shown by the photographic density of the yellow component at the unexposed portions.

DENSITY OF YELLOW COMPONENT AT UNEXPOSED PORTION

Layer containing Compound 14	Color printing paper A	Color printing paper B
Protective layer	0.06	0.05
Cyan layer	0.09	0.08
Ultraviolet absorbing layer or intermediate layer	0.10	0.08
Magenta layer	0.11	0.09
Intermediate layer	0.11	0.09
Yellow layer	0.11	0.09
Baryta layer	0.12	0.09
None	0.12	0.10

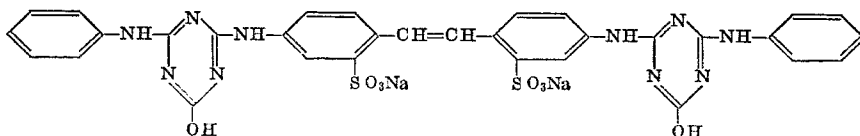
From these results, it can be seen that the best result was obtained when the fluorescent brightening agent was incorporated in the upper-most layer, or the protective layer. When the fluorescent brightening agent was incorporated in the lower layers more adjacent to the support, the effect was reduced the closer the layer was to the support. Also, it was shown that when the higher molecular weight fluorescent brightening agent of the present invention was incorporated in the uppermost layer of the color photographic printing paper, whitening of baryta became unnecessary.

Example 2

An alkaline aqueous solution of a yellow coupler, 3,5-dicarboxy - α - (4-stearoylamidobenzoyl)acetanilide, was added to a silver iodobromide emulsion and the blue-sensitive emulsion layer, thus prepared, was applied to a baryta-coated paper. To this emulsion layer was applied a green-sensitive silver chlorobromide emulsion containing a magenta coupler, 1-(3-sulfo-4-phenoxy)-3-stearoyl-5-pyrazolone. An emulsified dispersion of an ultraviolet absorber, Compounds 17-25 in dibutyl phthalate, was incorporated into a red-sensitive silver chlorobromide emulsion containing a cyan coupler, N-n-octadecyl-1-hydroxy-4-sulfo-2-1-naphthamide, and the resulting emulsion was applied to the green-sensitive emulsion layer. To the red-sensitive layer was further applied a protective layer at a thickness of 2.0 microns.

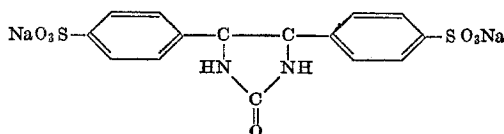
The above protective layer was formed by adding gradually a 4% dimethylformamide-water (1:1) solution of the high molecular weight fluorescent agent of this invention, Compounds 1-16, or known fluorescent brightening agents, Compound 26,

Compound 26



and Compound 27,

Compound 27



to an aqueous gelatin solution. The resulting mixture was applied to the red-sensitive emulsion layer so that the additives were present in an amount of 5 mg. per 100 cm.² of the protective layer.

After image exposure, the color printing papers thus prepared were developed in a developer containing N-ethyl-N- β -hydroxyethyl-p-phenylenediamine and then subjected to stop-fixing, washing, bleach-fixing, washing, hardening, washing, and drying procedures. The whiteness of the color printing papers thus processed is shown in the following table.

	Ultraviolet absorber									
Compound.....	17	18	19	20	21	22	23	24	25	
Fluorescent brightening agent:										
Compound:										
1-----	0.07	0.07	0.07	0.08	0.07	0.08	0.08	0.08	0.08	
2-----	0.07	0.07	0.07	0.08	0.07	0.08	0.08	0.08	0.08	
3-----	0.07	0.07	0.07	0.08	0.07	0.08	0.08	0.08	0.08	
4-----	0.07	0.07	0.07	0.08	0.07	0.08	0.08	0.08	0.08	
5-----	0.07	0.07	0.07	0.08	0.07	0.08	0.08	0.08	0.08	
6-----	0.07	0.07	0.07	0.08	0.07	0.08	0.08	0.08	0.08	
7-----	0.07	0.07	0.07	0.08	0.07	0.08	0.08	0.08	0.08	
8-----	0.07	0.07	0.07	0.08	0.07	0.08	0.08	0.08	0.08	
9-----	0.07	0.07	0.07	0.08	0.07	0.08	0.08	0.08	0.08	
10-----	0.07	0.07	0.07	0.08	0.07	0.08	0.08	0.08	0.08	
11-----	0.07	0.07	0.07	0.08	0.07	0.08	0.08	0.08	0.08	
12-----	0.06	0.06	0.06	0.07	0.06	0.07	0.07	0.07	0.07	
13-----	0.06	0.06	0.06	0.07	0.06	0.07	0.07	0.07	0.07	
14-----	0.06	0.06	0.06	0.07	0.06	0.07	0.07	0.07	0.07	
15-----	0.06	0.06	0.06	0.07	0.07	0.07	0.07	0.07	0.07	
16-----	0.06	0.06	0.06	0.07	0.07	0.07	0.07	0.07	0.07	
26-----	0.11	0.11	0.11	0.12	0.11	0.12	0.12	0.12	0.12	
27-----	0.11	0.11	0.11	0.12	0.11	0.12	0.12	0.12	0.12	
No additives	0.12	0.12	0.12	0.13	0.12	0.13	0.13	0.13	0.13	

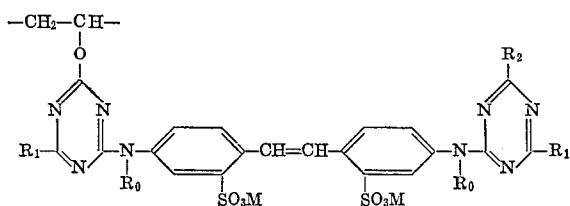
As can be seen from results shown in the above table, when the high molecular weight fluorescent brightening agent of the present invention was incorporated in the uppermost layer of the color photographic printing paper, a very remarkable brightening effect was obtained as compared to the use of conventionally known fluorescent brightening agents, i.e., Compound 26 or Compound 27, were incorporated in the uppermost layers, the compounds diffused out during the photographic processing and the brightening effect was reduced. Also, when the ultraviolet absorber was also employed in the present invention, the color photographic printing paper had an excellent fastness to light.

What is claimed is:

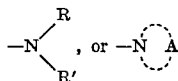
1. A color photographic printing paper comprising a support with multiple photographic layers, at least one of said layers containing an ultraviolet absorber and a fluorescent brightening agent or one of said layers closer to said support containing an ultraviolet absorber and a second layer farther away from said support containing a fluorescent brightening agent, provided that the layer containing said ultraviolet absorber is not a protective layer, said fluorescent brightening agent being a high mo-

13

lecular weight compound having repeating units represented by the general formula:



wherein R_0 is selected from the group consisting of a hydrogen atom, an alkyl group having from 1 to 8 carbon atoms, an aryl group having from 6 to 12 carbon atoms, a hydroxyalkyl group having from 2 to 4 carbon atoms, and a sulfoalkyl group having from 1 to 4 carbon atoms; wherein R_1 and R_2 each are selected from the group consisting of a halogen atom, —OR, —SR,



wherein R and R' each are selected from the group consisting of a hydrogen atom, an alkyl group having from 1 to 12 carbon atoms, a hydroxyalkyl group, a sulfoalkyl group, a carboxyalkyl group, an aralkyl group, an aryl group having from 6 to 18 carbon atoms, a substituted aryl group, or a cycloalkyl group having from 6 to 10 carbon atoms, or a substituted cycloalkyl group; and wherein A is selected from the group consisting of an alkylene group having from 4 to 5 carbon atoms, an alkylene group having a hetero atom and an alkylene group having a hetero atomic group; and M is selected from the group consisting of an alkali metal atom and an ammonium group.

2. The color photographic printing paper of claim 1, wherein said ultraviolet absorber and said fluorescent brightening agent are in separate photographic layers and wherein the fluorescent brightening agent is present in the photographic layer farthest away from the support.

3. The color photographic printing paper of claim 1, wherein said ultraviolet absorber is selected from the group consisting of a benzotriazole derivative, a benzophenone derivative, a thiazolidone derivative, a cinnamic acid ester, an oxathiazole derivative, a thiazole derivative, an imidazole derivative, an oxadiazole derivative, a thiadiazole derivative, a thiophene, a benzalazine derivative, and a bis-hydroxyarylamide compound.

4. The color photographic printing paper of claim 1, wherein said fluorescent brightening agent is present in the photographic layer in an amount of from 0.5 to 10 mg. per 100 cm.² of said photographic layer.

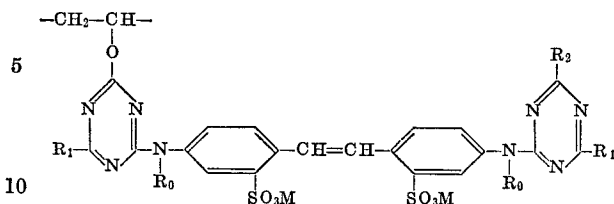
5. The color photographic printing paper of claim 4, wherein said ultraviolet absorber is present in the photographic layer in an amount of from 2 to 20 mg. per 100 cm.² of said photographic layer.

6. The color photographic printing paper of claim 1, wherein the fluorescent brightening agent has a molecular weight range of from 100,000 to 400,000.

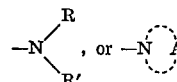
7. A color photographic printing paper which comprises a support having thereon, a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, and a red-sensitive silver halide emulsion layer, said paper having a layer containing a fluorescent brightening agent on the uppermost silver halide emulsion layer and said uppermost silver halide emulsion layer containing an ultraviolet absorber, said fluorescent brightening

14

agent being a high molecular weight compound having repeating units of the formula:

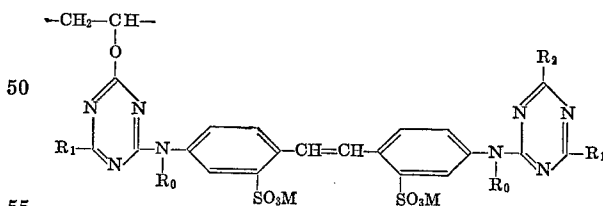


wherein R_0 is selected from the group consisting of a hydrogen atom, an alkyl group having from 1 to 8 carbon atoms, an aryl group having from 6 to 12 carbon atoms, a hydroxyalkyl group having from 2 to 4 carbon atoms, and a sulfoalkyl group having from 1 to 4 carbon atoms; wherein R_1 and R_2 each are selected from the group consisting of a halogen atom, —OR, —SR,

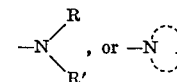


wherein R and R' each are selected from the group consisting of a hydrogen atom, an alkyl group having from 1 to 12 carbon atoms, a hydroxyalkyl group, a sulfoalkyl group, a carboxyalkyl group, an aralkyl group, an aryl group having from 6 to 18 carbon atoms, a substituted aryl group, or a cycloalkyl group having from 6 to 10 carbon atoms, or a substituted cycloalkyl group; and wherein A is selected from the group consisting of an alkylene group having from 4 to 5 carbon atoms, an alkylene group having a hetero atom and an alkylene group having a hetero atomic group; and M is selected from the group consisting of an alkali metal atom and an ammonium group.

8. A color photographic printing paper comprising a support having thereon, a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, and a red-sensitive silver halide emulsion layer, said paper having a layer containing a fluorescent brightening agent on the uppermost silver halide emulsion layer and having a layer containing an ultraviolet absorber between the uppermost silver halide emulsion layer and the middle silver emulsion layer, said fluorescent brightening agent being a high molecular weight compound having repeating units of the formula:



wherein R_0 is selected from the group consisting of a hydrogen atom, an alkyl group having from 1 to 8 carbon atoms, an aryl group having from 6 to 12 carbon atoms, a hydroxyalkyl group having from 2 to 4 carbon atoms, and a sulfoalkyl group having from 1 to 4 carbon atoms; wherein R_1 and R_2 each are selected from the group consisting of a halogen atom, —OR, —SR,

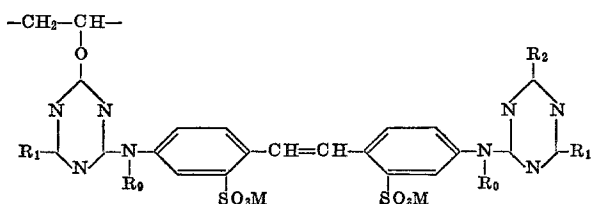


wherein R and R' each are selected from the group consisting of a hydrogen atom, an alkyl group having from 1 to 12 carbon atoms, a hydroxyalkyl group, a sulfoalkyl group, a carboxyalkyl group, an aralkyl group, an aryl group having from 6 to 18 carbon atoms, a substituted aryl group, or a cycloalkyl group having from 6 to 10 carbon atoms, or a substituted cycloalkyl group; and wherein A is selected from the group consisting of an alkylene group having from 4 to 5 carbon atoms, an alkylene group

15

having a hetero atom and an alkylene group having a hetero atomic group; and M is selected from the group consisting of an alkali metal atom and an ammonium group.

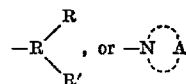
9. A color photographic printing paper comprising a support with multiple photographic layers, at least one of said layers containing an ultraviolet absorber and a fluorescent brightening agent or one of said layers closer to said support containing an ultraviolet absorber and a second layer farther away from said support containing a fluorescent brightening agent, provided that the layer containing said ultraviolet absorber is not a protective layer, said fluorescent brightening agent being a high molecular weight compound having repeating units of the formula:



wherein R₀ is selected from the group consisting of a hydrogen atom, an alkyl group having from 1 to 8 carbon atoms, an aryl group having from 6 to 12 carbon atoms, a hydroxyalkyl group having from 2 to 4 carbon atoms, and a sulfoalkyl group having from 1 to 4 carbon atoms;

16

wherein R₁ and R₂ each are selected from the group consisting of a halogen atom, —OR, —SR,

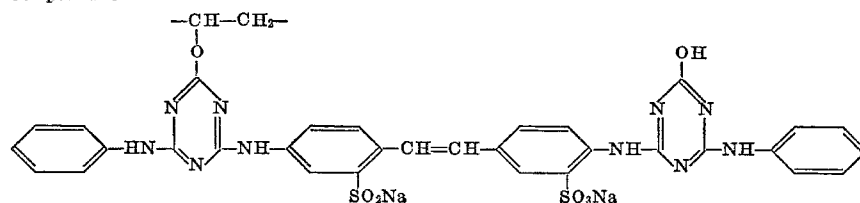


wherein R and R' each are selected from the group consisting of a hydrogen atom, an alkyl group having from 1 to 12 carbon atoms, a hydroxyalkyl group, a sulfoalkyl group, a carboxyalkyl group, an aralkyl group, an aryl group having from 6 to 18 carbon atoms, a substituted aryl group, or a cycloalkyl group having from 6 to 10 carbon atoms, or a substituted cycloalkyl group; and wherein A is selected from the group consisting of an alkylene group having from 4 to 5 carbon atoms, an alkylene group having a hetero atom and an alkylene group having a hetero atomic group; and M is selected from the group consisting of an alkali metal atom and an ammonium group,

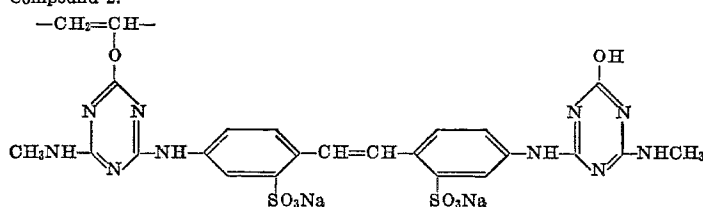
said ultraviolet absorber being a member selected from the group consisting of a benztriazole derivative, a benzophenone derivative, a thiazolidone derivative, a cinnamic acid ester, an oxathiazole derivative, a thiazole derivative, an imidazole derivative, an oxadiazole derivative, a thiadiazole derivative, a thiophene, a benzalazine derivative, and a bis-hydroxy-arylamide compound.

10. The color photographic printing paper of claim 1 wherein said fluorescent brightening agent is a member selected from the group consisting of:

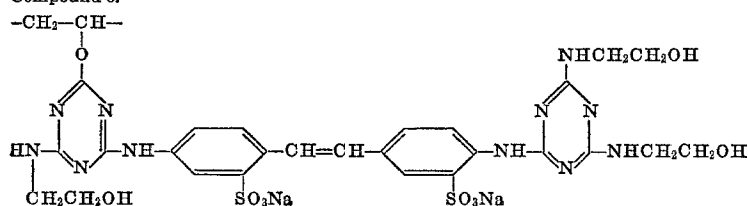
Compound 1:



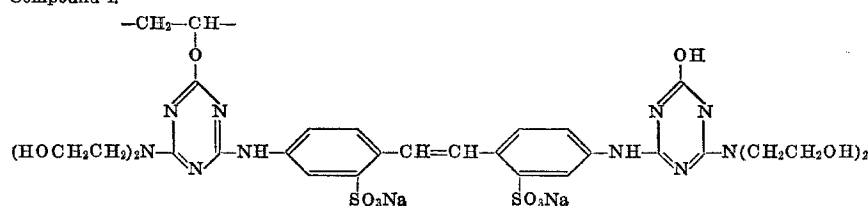
Compound 2:



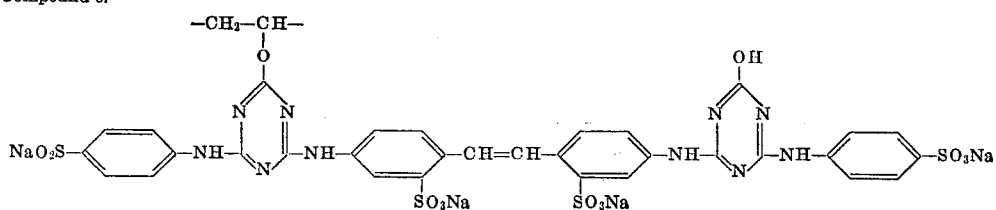
Compound 3:



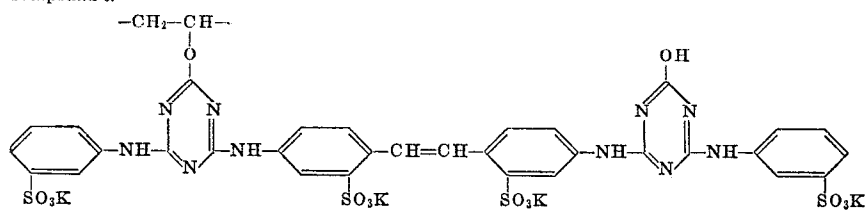
Compound 4:



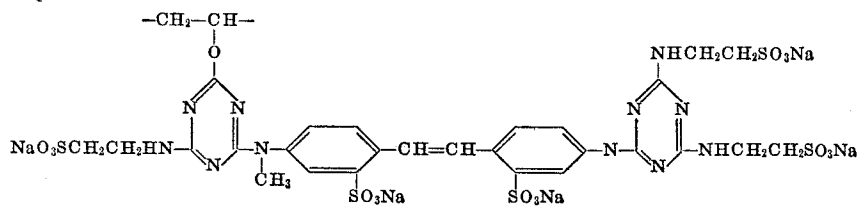
Compound 5:



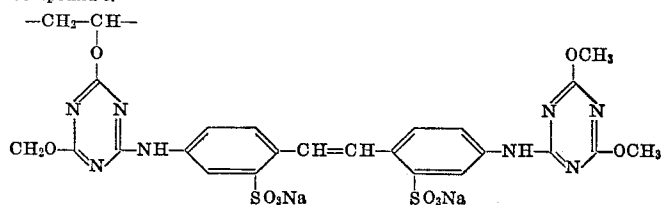
Compound 6:



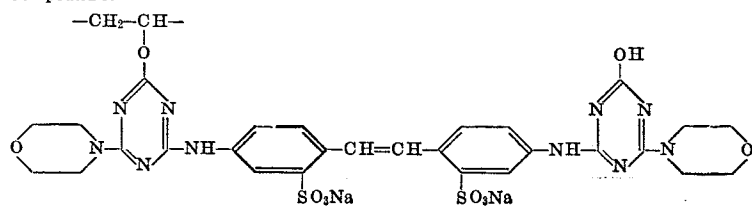
Compound 7:



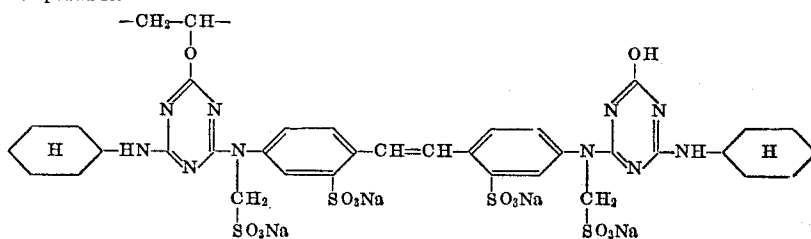
Compound 8:



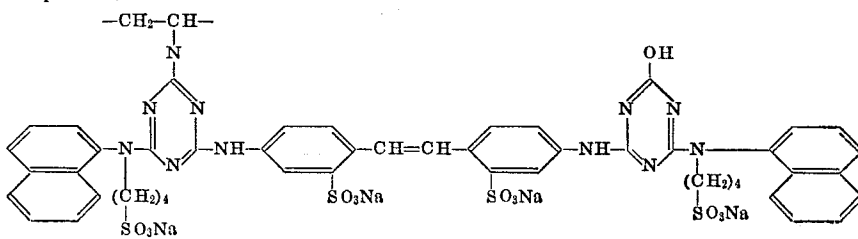
Compound 9:



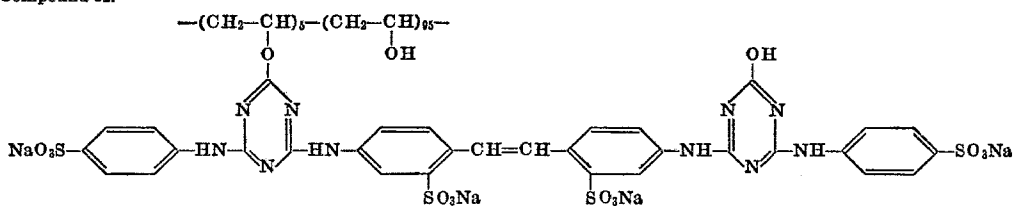
Compound 10:



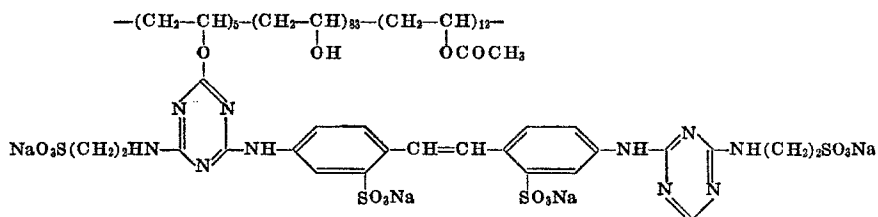
Compound 11:



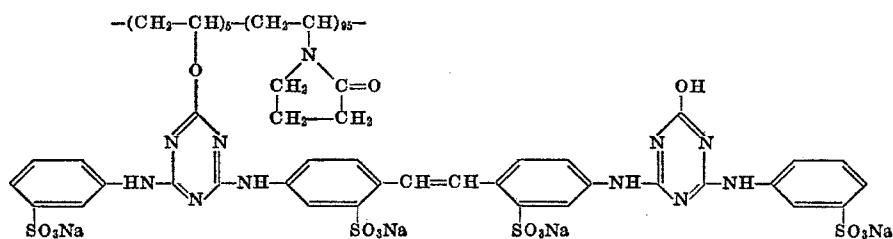
Compound 12:



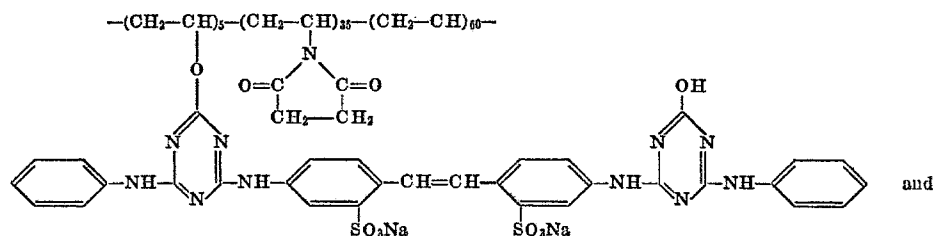
Compound 13:



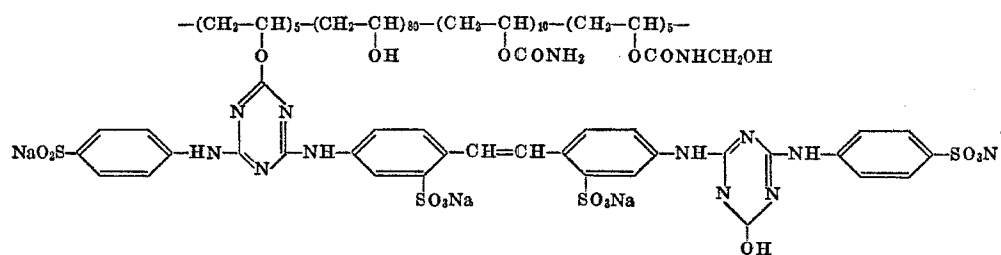
Compound 14



Compound 15

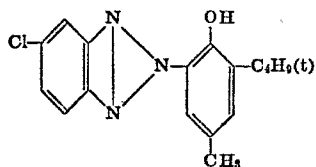


Compound 16

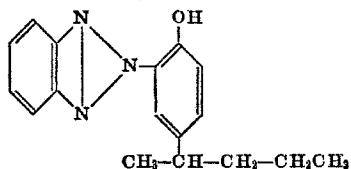


11. The color photographic printing paper of claim 1, wherein said ultraviolet absorber is a member selected from the group consisting of:

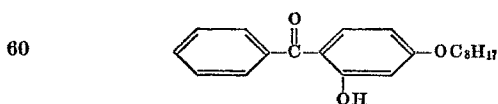
Compound 17:



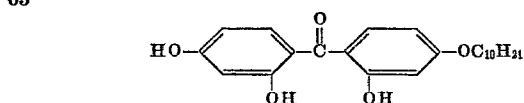
Compound 18:



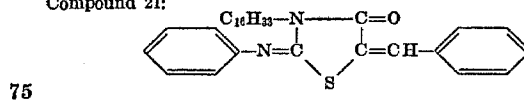
Compound 19:



Compound 20:

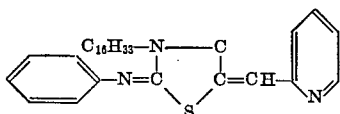


Compound 21:

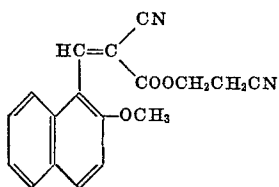


21

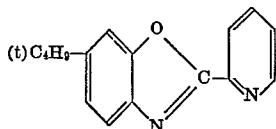
Compound 22:



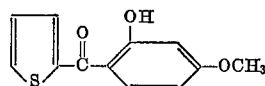
Compound 23:



Compound 24:

**22**

Compound 25:



- 5 **12.** The color photographic printing paper of claim 1, wherein the molecular weight of the fluorescent brightening agent ranges from about 20,000 to 1,000,000.

References Cited

10	UNITED STATES PATENTS			
	2,933,390	4/1960	McFall	96—100
	3,244,524	4/1966	Trucker	106—125
	3,269,840	8/1966	Pattyn	96—82
	3,365,293	1/1968	Haefeli	96—82
15	3,512,984	5/1970	Amano	96—82

NORMAN G. TORCHIN, Primary Examiner

J. R. HIGHTOWER, Assistant Examiner

20 U.S. Cl. X.R.
96—82, 84