

Sakamoto et al.

[45] **Apr. 16, 1974**

- | | | | |
|-----------|--------|-------------------|--------|
| 3,252,801 | 5/1966 | Cohen et al. | 96/114 |
|-----------|--------|-------------------|--------|

$$\begin{array}{c} R_1-N-C-SH \\ \diagdown \quad \diagup \\ N \quad N \\ \diagup \quad \diagdown \\ N \end{array} \quad \text{or} \quad \begin{array}{c} R_2-N-C-S-S-C-N-R_3 \\ \diagdown \quad \diagup \quad \quad \diagdown \quad \diagup \\ N \quad N \quad \quad N \quad N \\ \diagup \quad \diagdown \quad \quad \diagup \quad \diagdown \\ N \quad N \quad \quad N \end{array}$$

1 Claim, No Drawings

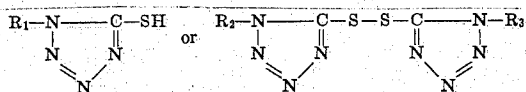
LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIAL

This invention relates to a light-sensitive silver halide photographic material improved in graininess of an image obtained by the development thereof.

It is well known that in order to improve a silver halide photographic material in graininess of the resulting image, the silver halide grains used in the photographic material should be made smaller in particle diameter. However, if a silver halide photographic material is made smaller in particle diameter of the silver halide grains used, the light sensitivity of the photographic material tends to be deteriorated accordingly, in general, causing the disadvantage that no desired sensitivity can be attained. With an aim to overcome such drawback, many efforts have heretofore been made by using specific chemicals or by varying the time and temperature for the preparation of silver halides, but no sufficiently satisfactory process has yet been found. Further, for the improvement in graininess of a light-sensitive silver halide color photographic material, there have been known a method in which the number of silver halide grains is increased, and a method in which a specific chemical is incorporated into the color photographic emulsion to lower the color developability thereof. However, the former method has such drawbacks that the expensive silver halide is required in large quantities, so that the photographic material becomes high in cost and, at the same time, the formation of fog becomes easy, while the latter method has such drawbacks that the effect of the chemical incorporated varies depending on the kind of coupler used, so that the coupler to be used in combination therewith is limited, or there is brought about marked desensitization.

We have found a novel process for improving graininess which process is entirely free from the above-mentioned drawbacks of the prior art processes. According to the process of the present invention, it is possible to obtain a light-sensitive silver halide photographic material which has less tendency to fogging without sacrificing the sensitivity and which has been greatly improved in graininess.

That is, the present invention provides a light-sensitive silver halide photographic material excellent in graininess which has been prepared by use of a silver halide photographic material incorporated with the combination of (I) a poly-N-vinylpyrrolidone or a copolymer containing a N-vinylpyrrolidone unit and (II) a compound (hereinafter referred to as "mercaptotetrazole compound") of the general formula (II),



wherein R_1 , R_2 and R_3 are individually a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an aryl group or an aralkyl group, and R_2 and R_3 may be the same or different.

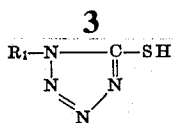
The process of the present invention is effectively applicable to any light-sensitive silver halide black-and-white and color photographic materials, but particularly marked effects are observed when the process is applied to the color photographic materials.

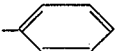
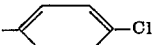
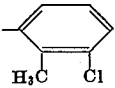
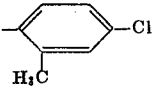
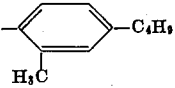
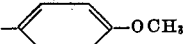
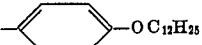
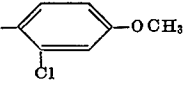
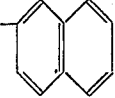
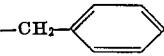
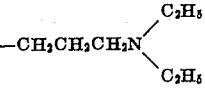
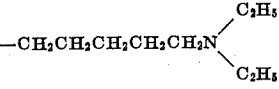
Examples of high polymers and mercaptotetrazole compounds usable in the present invention are shown below, though these are not limitative.

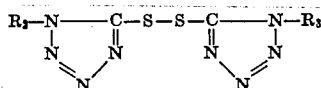
Examples of high polymers (I):

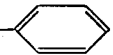
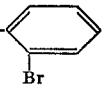
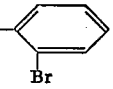
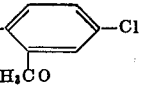
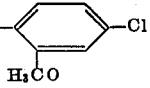
Compound	Monomer ratio
(I)-1 Poly-N-vinyl-2-pyrrolidone	
(I)-2 N-Vinylpyrrolidone/imidazolinoacrylic acid amide copolymer	42:58
(I)-3 N-Vinylpyrrolidone/morpholinoacrylic acid amide copolymer	42:58
(I)-4 N-Vinylpyrrolidone/piperidinoacrylic acid amide copolymer	42:58
(I)-5 N-Vinylpyrrolidone/2-methylimidazolinoacrylic acid amide copolymer	42:58
(I)-6 N-Vinylpyrrolidone/acrylic acid diethylamide copolymer	42:58
(I)-7 N-Vinylpyrrolidone/sodium acrylate copolymer	75:25
(I)-8 N-Vinylpyrrolidone/methyl acrylate copolymer	42:58
(I)-9 N-Vinylpyrrolidone/acrylic acid amide copolymer	75:25
(I)-10 N-Vinylpyrrolidone/ethyl acrylate copolymer	70:30
(I)-11 N-Vinylpyrrolidone/acrylic acid amide/ammonium maleamate copolymer	40:40:20
(I)-12 N-Vinylpyrrolidone/acrylic acid amide/maleic anhydride copolymer	40:40:20
(I)-13 N-Vinylpyrrolidone/acrylic acid amide/2-methylimidazole copolymer	60:20:20
(I)-14 N-Vinylpyrrolidone/acrylic acid amide/sodium 2-methylimidazole-3-hydropropionate copolymer	60:20:20
(I)-15 N-Vinylpyrrolidone/imidazole imadazolinomaleamate copolymer	60:40
(I)-16 N-Vinylpyrrolidone/2-methylimidazole 2-methylimidazolino-maleamate copolymer	60:40
(I)-17 N-Vinylpyrrolidone/2-methylimidazole copolymer	60:40
(I)-18 N-Vinylpyrrolidone/morpholino-methacrylic acid/methyl methacrylate copolymer	20:20:60
(I)-19 N-Vinylpyrrolidone/4-vinylpyridino-N-methyl iodide copolymer	42:58
(I)-20 N-Vinylpyrrolidone/piperidine 60:40 piperidinomaleamate copolymer	
(I)-21 N-Vinylpyrrolidone/thiourea half-ammonium maleate copolymer	60:40
(I)-22 N-Vinylpyrrolidone/styrene copolymer	70:30
(I)-23 N-Vinylpyrrolidone/piperidino methacrylate/methyl methacrylate copolymer	20:20:60
(I)-24 N-Vinylpyrrolidone/methacrylic acid amide/methyl methacrylate copolymer	20:20:60
(I)-25 N-Vinylpyrrolidone/vinyl acetate copolymer	70:30

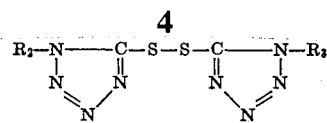
Examples of mercaptotetrazole compounds:

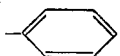
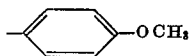
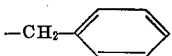
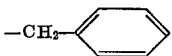
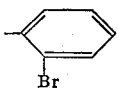
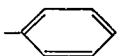


Compound	R ₁
(II)-1.....	-H
(II)-2.....	-CH ₃
(II)-3.....	-CH ₂ -CH=CH ₂
(II)-4.....	
(II)-5.....	
(II)-6.....	
(II)-7.....	
(II)-8.....	
(II)-9.....	
(II)-10.....	
(II)-11.....	
(II)-12.....	
(II)-13.....	
(II)-14.....	
(II)-15.....	-CH ₂ -(CH ₂) ₇ -CH=CH(CH ₂) ₇ -CH ₃
(II)-16.....	-C ₁₇ H ₃₅
(II)-17.....	-CH ₂ COOC ₂ H ₅
(II)-18.....	
(II)-19.....	



Compound	R ₂	R ₃
(II)-20.....	-H	-H
(II)-21.....	-C ₂ H ₅	-C ₂ H ₅
(II)-22.....		
(II)-23.....		
(II)-24.....		



Compound	R ₂	R ₃
(II)-25.....		
(II)-26.....		
(II)-27.....		
(II)-28.....	-C ₁₈ H ₃₅	-C ₁₈ H ₃₅

Among the high polymers used in the present invention, all the copolymers containing vinylpyrrolidone can display marked graininess-improving effects when used in combination with the mercaptotetrazole compounds, though the degrees of said effects vary depending on the monomer ratios.

If necessary, the above-mentioned high polymers and mercaptotetrazole compounds may individually be used in the form of mixtures of two or more. The high polymer and mercapto compound may be incorporated into one emulsion layer, and may be incorporated not only into emulsion layers adjacent to each other but also into such auxiliary layer as sub layer, inter layer or protective layer. These compounds may be incorporated into a silver halide emulsion at any step during the preparation of the silver halide emulsion, but it is more effective to incorporate the compounds during the second ripening, or prior to coating, of the silver halide emulsion.

In case the compounds are desired to be incorporated during the second ripening of the silver halide emulsion, the temperature and time of the second ripening should be selected properly, whereby excellent photographic properties can be imparted to the resulting light-sensitive photographic material. In the case of a light-sensitive color photographic material using an oil-soluble coupler, the compounds may be incorporated into the coupler dispersion.

The amounts of the compounds to be incorporated vary depending on the kinds of said compounds, but it is particularly effective to incorporate the high polymer in an amount of 0.2 to 100 g., and the mercaptotetrazole compound in an amount of 0.001 to 10 g., per mole of AgX. The high polymer is desirably one which is soluble in water or alkali. If the high polymer is not soluble in said liquid, it is dissolved in a solvent such as methanol, ethanol, acetone, ethyl acetate, dioxane, dimethylformamide or the like, and the resulting solution is added to a silver halide emulsion or inter layer-forming liquid. On the other hand, the mercaptotetrazole compound may also be dissolved in the same manner as in the case of the high polymer, and the resulting solution is added to a silver halide emulsion or auxiliary layer-forming liquid.

The photographic emulsions used in the present invention include emulsions of AgCl, AgBr, AgClBr, AgBrI, etc. These emulsions may have been optically sensitized with cyanine and merocyanine compounds, and may have been subjected to chemical sensitization treatments using sulfur-containing compounds, noble metal salts, polyalkylene oxide derivatives or reducing compounds.

Further, formalin and the like may be used as hardeners, and synthetic surface active agents or natural surface active compounds, e.g. saponin and the like, may be used as coating aids. As couplers applicable to the case of light-sensitive color photographic materials, there may be used those which can produce a color image by means of p-phenylenediamine type color developers. Examples of these couplers are yellow couplers having benzoyl acetanilide groups, magenta couplers having a pyrazolone or indazolone nucleus or a cyanoacetyl group and cyan couplers having a phenol or naphthol nucleus. These couplers may contain in the active methylene- or methine-portions a substituent capable of releasing by color development reaction such as, for example, halogens, or arylazo, aryloxy or arylthio groups. Further, these couplers may contain in the molecule either one or both of a non-diffusible group such as, for example, a long chain alkyl group or an alkylphenoxy group, and a water-solubilizing group such as, for example, a sulfonic group or a carboxyl group. Among these couplers, those which are oleophilic are dissolved in a high boiling organic solvent, e.g. dibutyl phthalate, or in a low boiling organic solvent, e.g. chloroform, acetone or dimethylformamide, and the resulting solutions are formed into dispersions. Further, water-soluble couplers are dissolved in alkali or the like, and the resulting solutions may be added directly to silver halide emulsions or incorporated into color developers.

In the case of the light-sensitive color photographic material of the present invention, the light sensitive layer may be composed of protective layer, yellow layer, yellow filter layer, magenta layer, inter layer, cyan layer, antihalation layer and support in this order from the upper-most layer, or may be composed of magenta, cyan and yellow layers in this order, though the order varies depending on the intended application of the photographic material. Further, the color developing layer may be composed of one or 2 layers.

As the support for use in the present invention, there is ordinarily used a paper or a natural or synthetic high polymer films of the cellulose acetate or polyester type.

In case the thus obtained light-sensitive photographic material according to the present invention is a black-white photographic material, it may be developed by treatment with a solution containing Metol, hydroquinone and phenidone, while in case the photographic material is a color photographic material, it may be developed by using a color developer of the p-phenylenediamine type to form a color image directly by the first development, as in the case of a color negative, or it may be subjected to black-white development using Metol and hydroquinone and then to treatment for forming a color image, like the reversal color treatment.

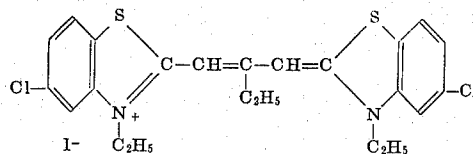
Typical examples of the black-white developing agent used for development of the light-sensitive photographic material according to the present invention are hydroquinone, p-phenylenediamine, p-aminophenol, Metol, pyrogallol, amidol, glycine and 1-phenyl-3-pyrazolidone. Typical examples of the color developing agent are sulfates, chlorides and sulfites of N,N-diethyl-p-phenylenediamine, N-ethyl-N-hydroxyethyl-p-phenylenediamine, N-ethyl-N-hydroxyethyl-p-phenylenediamine, N-ethyl-N-hydroxyethyl-2-methyl-p-phenylenediamine and N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline.

The present invention is applicable also to mixed packet type light-sensitive color photographic materials and DTR method light-sensitive materials.

The present invention is illustrated in further detail below with reference to examples, but the scope of the invention is not limited to these examples.

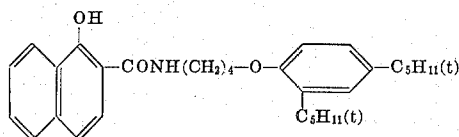
EXAMPLE 1

A high speed light-sensitive gelatinous silver iodobromide emulsion containing 3.5 mole percent of AgI and 160 g. of gelatin per mole of AgX was subjected to second ripening, and incorporated with 0.18 g. per mole of AgX of a spectral sensitizing dye of the structure,

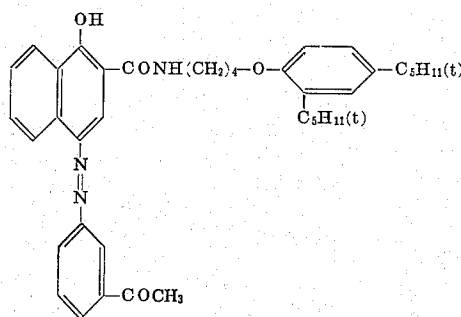


to prepare a red-sensitive emulsions. This emulsion was incorporated with the high polymer (I)-1 and the mercaptotetrazole compound (II)-4 in such a combination as shown in Table 1. Thereafter, two kinds of couplers of the structures shown below were subjected to a high speed rotary mixer to form a dispersion.

Coupler (1):



Coupler (2):



In this case, the composition of the coupler dispersion was as shown below in which the amount of each constituent is per mole of AgX.

Formulation of coupler dispersion:

Coupler (1)	10 g.
Coupler (2)	4 g.
2,5-Di-(t)-octyl hydroquinone	0.5 g.
Tricresyl phosphate	20 g.
Ethyl acetate	30 g.
5% Alkanol B (trade mark of Du Pont)	15 ml.
3% Gelatin	400 ml.

This coupler dispersion was mixed with the aforesaid emulsion, to which were then added, per mole of AgX, 150 ml. of 1 percent formalin and 300 ml. of saponin. Subsequently, the emulsion was coated on a cellulose triacetate film base to a dry film thickness of 3.5 μ and then dried to prepare a light-sensitive photographic material. This photographic material was exposed through an optical wedge to a definite light and then

subjected to the following color development treatment:

- (1) Color development, 20°C., 12 minutes:

Formulation of developer:

Benzyl alcohol

3.8 ml.

Anhydrous sodium sulfite

2.0 g.

N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate

5.0 g.

Sodium carbonate (monohydrate)

50.0 g.

Potassium bromide

1.0 g.

Water to make

1,000 ml.

(Adjusted to pH 10.8 by addition of caustic soda or sulfuric acid)

(2) Stop Bath, 20°C., 4 minutes:

Formulation of stop solution:

Glacial acetic acid

30 ml.

Sodium hydroxide

1.6 g.

Water to make

1,000 ml.

(3) First fixing, 20°C., 5 minutes:

Formulation of fixing bath:

Sodium thiosulfate

150 g.

Water to make

1,000 ml.

(4) Water-washing, 5 minutes.

(5) Bleaching, 5 minutes:

Formulation of bleaching bath:

Potassium ferrocyanide

100.0 g.

Potassium bromide

50.0 g.

Water to make

1,000 ml.

(6) Water-washing, 5 minutes.

(7) Second fixing, 20°C., 5 minutes:

Formulation of the fixing bath was same as in the first fixing bath.

(8) Water-washing, 10 minutes.

(9) Drying.

The relative speed, fog and RMS graininess at the point of color image density value of 0.3 in the developed photographic materials were as set forth in Table 1. (The RMS graininess referred to herein is a value of 1,000 times the standard deviation of variations in density value observed when a sample, which has been exposed and developed under definite conditions, is scanned by means of a microdensitometer having circular scanning openings of 2.5 μ in diameter.)

Table 1

Amount of high polymer incorporated (g/mole AgX)	Amount of mercapto-tetrazole compound incorporated (g/mole AgX)	Relative speed	Fog	RMS
—	—	100	0.16	81
(I)-1 4.5 g.	—	103	0.17	78
(I)-1 9.0 g.	—	100	0.16	78
—	(II)-4 0.006 g.	98	0.13	75
—	(II)-4 0.12 g.	93	0.10	75
(I)-1 4.5 g.	(II)-4 0.06 g.	99	0.08	63
(I)-1 4.5 g.	(II)-4 0.12 g.	96	0.08	54
(I)-1 9.0 g.	(II)-4 0.06 g.	98	0.08	58
(I)-1 9.0 g.	(II)-4 0.12 g.	95	0.06	51

From Table 1, it is clear that the photographic materials of the present invention are markedly low in RMS value without any substantial desensitization, and thus have been greatly improved in graininess.

EXAMPLE 2

The red-sensitive emulsion used in Example 1 was mixed with a coupler dispersion of the composition shown below. The amount of each constituent of the coupler dispersion was per mole of AgX.

Composition of coupler dispersion

(1)

Composition of coupler dispersion

(2)

Coupler (2)	45 g.	45 g.
Tricresyl phosphate	30 g.	30 g.
Ethyl acetate	50 g.	50 g.
Compound (II)-10	—	0.3 g.
3% Gelatin	300 ml.	300 ml.
5% Alkanol B	50 ml.	50 ml.
High polymer (I)-5	—	10 g.

To the emulsion were then added, per mole of AgX, 120 ml. of 1 percent formalin and 300 ml. of 5 percent saponin. Subsequently, the emulsion was coated on a cellulose triacetate film base to a dry film thickness of 5 μ and then dried to prepare a light-sensitive photographic material. This photographic material was subjected to the same development treatment as in Example 1 to obtain the results set forth in Table 2.

Table 2

	Relative speed	Fog	RMS
Photographic material containing coupler dispersion (1)	100	0.13	88
Photographic material containing coupler dispersion (2)	101	0.11	65

From Table 2, it is understood that a marked graininess-improving effect can be attained also in the case where a coupler dispersion incorporated with the high polymer and mercaptotetrazole compound is added to a photographic emulsion.

EXAMPLE 3

Each of the two light-sensitive photographic materials prepared in Example (2) was exposed to a definite light and then subjected to reversal treatment using Kodak Process E IV-Kit (Trademark of Eastman Kodak Co.).

Reversal treatment conditions:

1. Prehardening	29.5°C., 3 minutes
2. Neutralization	29.5°C., 1 minute
3. First development	29.5°C., 7 minutes
4. First stopping	29.5°C., 2 minutes
5. Water-washing	27-32°C., 4 minutes
6. Color development	29.5°C., 15 minutes
7. Second stopping	29.5°C., 3 minutes
8. Water-washing	27-32°C., 3 minutes
9. Bleaching	29.5°C., 5 minutes
10. Fixing	29.5°C., 6 minutes
11. Water-washing	27-32°C., 6 minutes
12. Stabilization	29.5°C., 1 minute

The results of the reversal treatment were as set forth in Table 3, in which RMS graininess is a value measured at the point of a color density value of 1.0.

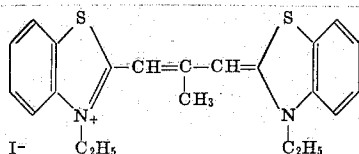
Table 3

	Relative speed	RMS
Photographic material containing coupler dispersion (1)	100	69
Photographic material containing coupler dispersion (2)	96	56

As seen in Table 3, a graininess-improving effect is clearly observed also in reversal color development treatment.

9 EXAMPLE 4

A high speed light-sensitive gelatinous silver iodobromide photographic emulsion containing 5.0 mole percent of AgI, and 120 g. of gelatin per mole of AgX was subjected to second ripening, and incorporated with 0.20 g. per mole of AgX of a spectral sensitizing dye of the structure shown below and 1.8 g. per mole of AgX of 5-methyl-7-hydroxy-1,3,4-triazaindolizine to prepare a panchromatic emulsion. Spectral sensitizing dye:



This emulsion was incorporated with the high polymer (I)-16 and the mercaptotetrazole compound (II)-9 in such a combination as shown in Table 4. To the emulsion were then added, per mole of AgX, 100 ml. of 1 percent formalin and 200 ml. of 5 percent saponin. Subsequently, the emulsion was coated on a cellulose triacetate film base to a dry film thickness of 4 μ and then dried to prepare a photographic material. This photographic material was exposed through an optical wedge to a definite light and then subjected to the following black-white development treatment:

(1) Development, 20°C., 9 minutes:

Formulation of developer:

Water	500 ml.
Metol	1.5 g.
Anhydrous sodium sulfite	100 g.
Hydroquinone	3 g.
Konigrain (trade mark of Konishiroku Photo Industry Co., Ltd.)	2 g.
Potassium bromide	0.5 g.
Water to make	1,000 ml.

(2) Fixing, 20°C., 6 minutes:

Formulation of fixing solution:

Solution A	Water	600 ml.
	Sodium thiosulfate	250 g.
	Water	200 ml.
	Anhydrous sodium sulfite	15 g.
Solution B	Acetic acid (23%)	58 ml.
	Konigrain	13.5 g.
	Potassium alum	15 g.

(The solution B was gradually added to the solution A with stirring, and the mixed solution was used as it was.)

(3) Water-washing, 15 minutes.

(4) Drying.

The results of the development were as set forth in Table 4, in which the RMS granularity is a value measured at the point of a density value of 1.0.

Table 4

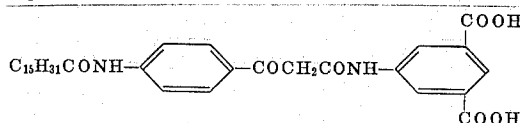
Amount of high polymer incorporated (g/mole AgX)	Amount of mercaptotetrazole compound incorporated (g/mole AgX)	Relative speed	Fog	RMS
—	—	100	0.08	86
(I)-16 2 g.	—	101	0.09	86
—	(II)-9 0.08 g.	98	0.06	83
(I)-16 2 g.	(II)-9 0.08 g.	98	0.05	79

As seen in Table 4, the effect of the present invention is displayed also in the case of a light-sensitive black-white photographic material.

10 EXAMPLE 5

A high speed light-sensitive gelatinous silver iodobromide photographic emulsion containing 2 mole percent of AgI and 160 g. of gelatin per mole of AgX was subjected to second ripening, and incorporated with 1.4 g. per mole of AgX of 5-methyl-7-hydroxy-1,3,4-triazaindolizine to prepare a blue-sensitive photographic emulsion. This emulsion was incorporated with the combination of high polymer and mercaptotetrazole compound as shown in Table 5. Thereafter, 75 g. of a coupler (3) of the structure shown below was dissolved in caustic soda and water, and then mixed with the emulsion.

Coupler (3):



To the emulsion were then added, per mole of AgX, 100 ml. of 1 percent formalin and 300 ml. of 5 percent saponin. Subsequently, the emulsion was coated on a cellulose triacetate film base to a dry film thickness of 5 μ and then dried to prepare a light-sensitive photographic material. This photographic material was exposed to a definite light and then developed at 20°C. for 10 minutes with a developer of the following formulation:

Formulation of developer:

Anhydrous sodium sulfite	2.0 g.
4-Amino-N,N-diethylaniline hydrochloride	5.0 g.
Sodium carbonate (monohydrate)	50.0 g.
Potassium bromide	1.0 g.
Water to make	1,000 ml.

The results obtained were as set forth in Table 5. After the color development, the same treatments as in Example 1 were effected.

Table 5

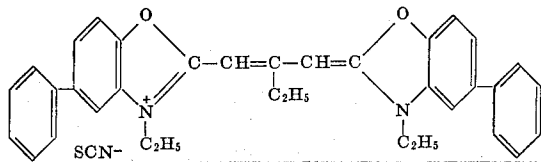
Amount of high polymer incorporated (g/mole AgX)	Amount of mercaptotetrazole compound incorporated (g/mole AgX)	Relative speed	Fog	RMS
—	—	100	0.11	88
(I)-3 3 g.	(II)-9 0.08 g.	96	0.09	76
(I)-5 3 g.	(II)-9 0.08 g.	100	0.12	69
(I)-9 3 g.	(II)-9 0.08 g.	102	0.11	71
(I)-20 3 g.	(II)-2 0.08 g.	95	0.07	68
(I)-20 3 g.	(II)-12 0.08 g.	98	0.11	70
(I)-20 3 g.	(II)-13 0.08 g.	98	0.10	72

As is clear from Table 5, the combination use of high polymer and mercaptotetrazole compound results in marked improvement in graininess.

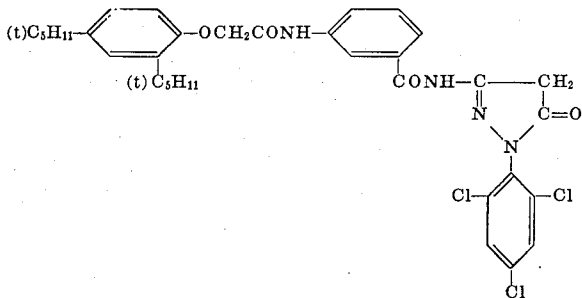
EXAMPLE 6

A high speed light-sensitive gelatinous silver iodobromide photographic emulsion containing 4.5 mole percent of AgI, and 160 g. of gelatin per mole of AgX was subjected to second ripening, and incorporated with 0.13 g. per mole of AgX of a spectral sensitizing dye of the structure shown below and 1.4 g. per mole of AgX of 5-methyl-7-hydroxy-1,3,4-triazaindolizine to prepare a green-sensitive photographic emulsion. Spectral sensitizing dye:

11



This emulsion was incorporated with a high polymer and a mercaptotetrazole compound in such a combination as shown in Table 6. Thereafter, a coupler (4) of the structure shown below was subjected to a high speed rotary mixer to form a dispersion.
Coupler (4):



The composition of the coupler dispersion was as shown below in which the amount of each constituent is per mole of AgX.

Composition of coupler dispersion:	
Coupler (4)	40 g.
Tricresyl phosphate	20 g.
Ethyl acetate	250 g.
5% Alkanol B	120 ml.
3% Gelatin	1,000 ml.

The above-mentioned coupler dispersion was mixed with the aforesaid emulsion to which were then added, per mole of AgX, 90 ml. of 1 percent formalin and 300 ml. of 5 percent saponin. Subsequently, the emulsion was coated on a cellulose triacetate film base to a dry film thickness of 5 μ and then dried to prepare a light-sensitive photographic material. This photographic ma-

12

terial was subjected to the same development treatment as in Example 1 to obtain the results set forth in Table 6.

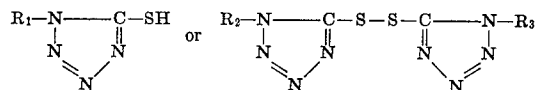
Table 6

Amount of high polymer incorporated (g/mole AgX)	Amount of mercaptotetrazole compound incorporated (g/mole AgX)	Relative speed	Fog	RMS
—	—	100	0.08	86
(I)—1 6 g.	(II)—4 0.02 g.	101	0.09	69
(I)—8 3 g.	(II)—13 0.02 g.			
(I)—3 3 g.	(II)—22 0.04 g.	97	0.06	65

As seen in Table 6, a marked graininess-improving effect is observed also in the case where there is used a combination of one high polymer and two mercaptotetrazole compounds or of two high polymers and one mercaptotetrazole compound.

What we claim is:

1. A light-sensitive silver halide photographic material containing in any of the layers thereof a combination of a N-vinylpyrrolidone polymer or copolymer containing a N-vinyl-pyrrolidone unit with a mercaptotetrazole compound of the general formula,



wherein R_1 , R_2 and R_3 are individually a hydrogen atom, an alkyl, alkenyl or alkynyl group, or an aryl or aralkyl group, and R_2 and R_3 may be same or different and wherein the N-vinyl-pyrrolidone polymer or copolymer is used in an amount of 0.2 g. to 100 g. per mole of silver halide contained therein and the mercaptotetrazole compound is used in an amount of 0.001 g. to 10 g. per mole of silver halide which material comprises a binder consisting essentially of gelatin and the polymer or copolymer of N-vinylpyrrolidone.

* * * * *