

# PATENT SPECIFICATION

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## (54) LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIAL AND METHOD OF PROCESSING THEREOF

(71) We, KONISHIROKU PHOTO INDUSTRY CO. LTD., a Corporation organized and existing under the laws of Japan, of 1—10, 3-chome, Nihonbashi-muromachi, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a novel light-sensitive silver halide photographic material and the processing method therefor. Particularly, it relates to a novel lith type light sensitive silver halide photographic material for obtaining a photographic image with an especially high contrast, high sharpness and high resolving power, and to the processing method therefor.

More particularly, it relates to a novel light-sensitive silver halide photographic material which is applicable advantageously to a light-sensitive silver halide photographic material with a high contrast suitable for forming a dot- or line-image on a lith (printing) light-sensitive silver halide material or a copying light-sensitive material, as well as to the processing method therefor.

It has been known to form a photographic image with an extremely high contrast by using some kind of a light-sensitive silver halide photographic material.

It has been known, for example, to obtain a high contrast image, e.g. a line- or dot-image, by treating, with an alkaline hydroquinones developing solution containing sulfite ions in a very low concentration, a light-sensitive material which comprises a silver halide emulsion containing silver chloride in a high content (at least more than 50 mole %) and further containing silver iodide less than 5 mole %, the grains of which emulsion being minute (average grain size; ca. 0.3  $\mu$ ), uniform in size and shape, and the grain size distribution thereof being narrow. The above-mentioned kind of light-sensitive silver halide material is known as the lith type light-sensitive material.

In printing business, there is usually required such a process as to convert a continuous gradation original image to a dot image, i.e. a process to convert the densities of the continuous gradation to a predetermined numbered assembly of dots respectively having area of the same densities but proportional in size to the densities of the continuous gradation. In order to carry out this, the lith type light-sensitive material is subjected to development, after photographing the original image through a cross- or contract-screen, to form the dot image on the light-sensitive material.

For this purpose there has been employed a light-sensitive silver halide photographic material containing a silver halide emulsion, the grains of which being minute and being uniform in size and shape. Even when this kind of a light-sensitive silver halide photographic material is employed, the intermediate density region (undesired continuous gradation parts) is reproduced, beside the maximum density region and the minimum one (fog), when the material is processed with a standard black and white developing solution. The intermediate density region or the so-called flinge is undesirable for producing printing plates and makes the dot quality worse.

There has heretofore been employed on the lith type light-sensitive material also for the reproduction of a line image. For the same reason, however, there have been obtained images having at best the  $\gamma$ -value of 5 — 6 of the characteristic

curve, which value is lower than 7—9 required for forming the desirable line image, if the standard black and white developing solution is employed. In order to avoid this, there has been employed, as mentioned above, a specific developing solution called "an infectious developing solution." It is indispensable, however, to maintain the sulfite concentration in the infectious developing solution as low as possible to obtain a high contrast image, but such a developing solution has very poor storability because of the low concentration of the sulfite. Every effort has been made, however, to improve the storability. Nevertheless, such efforts have not been so successful. As a result, an ordinary developing solution for continuous gradation, such as a Metol/hydroquinone or 1 - phenyl - 3 - pyrazolidone/hydroquinone developing solution, which has excellent storability, is recommended for processing the lith light-sensitive materials. However, there has been known no method capable of obtaining a dot image with a good dot quality, by using such the developing solution.

This invention provides a light-sensitive silver halide photographic material which comprises a support, at least one hydrophilic colloidal layer coated thereon containing silver halide grains having a number average grain size of from 0.1 to 0.5 $\mu$ , at least 80% of which grains are within a range of from 0.7 to 1.3 times said average grain size, and the silver halide being silver chlorobromide or chloriodobromide containing at least 50 mole% of silver chloride, and a tetrazolium compound of the formula (I), (II) or (III) as set out below.

The invention also provides a method of processing these photographic materials, after image-wise exposure to light, by contacting the resulting exposed photographic material with a hydroquinone-containing developing solution.

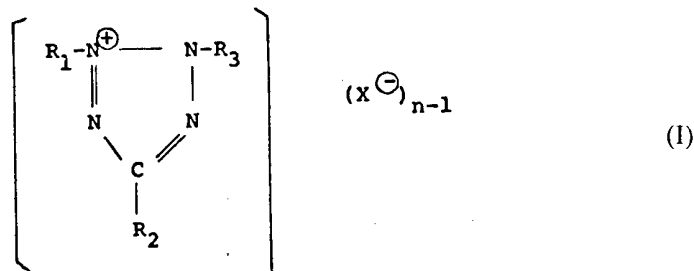
In accordance with the invention, there is thus formed a superior line- or dot-image, without employing infectious development.

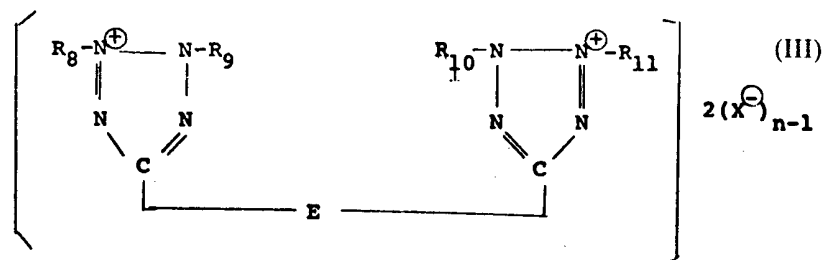
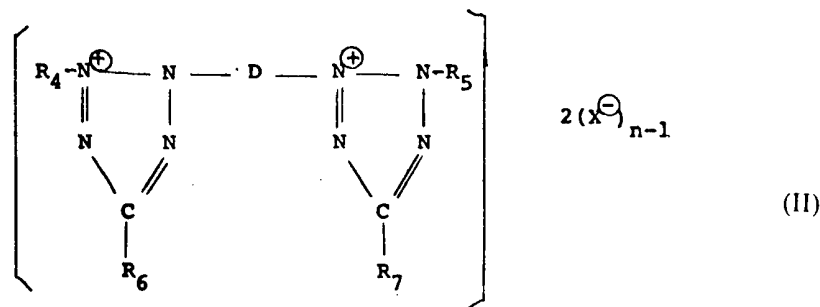
According to another preferred embodiment of the invention, there is obtained a dot-image (half tone image) with a superior dot quality by developing a light-sensitive silver halide photographic material containing the silver halide of the invention and a non-diffusible tetrazolium compound after the image exposure through a contact screen, with the Metol/hydroquinone developing solution (hereinafter referred to as the MQ developing solution) or with the 1 - phenyl - 3 - pyrazolidone/hydroquinone developing solution (hereinafter referred to as the PQ developing solution) which are widely used black and white developing solutions.

It cannot be expected from heretofore known techniques that high contrast line- or dot-images could be obtained without employing the infectious developing solution.

As explained above, the tetrazolium compounds include non-diffusible and diffusible ones. The term "non-diffusible tetrazolium compound" means a compound which does not dissolve from the light-sensitive material into the developing solution during the development. In other words, the compound preferably does not dissolve in a concentration of more than 2%, when a gelatin layer containing the compound is dipped for 10 minutes in an aqueous solution at 20—40°C having the same ion strength and pH-value as those of the developing solution.

The tetrazolium compounds employed in the invention have the general formulae:





In the above formulae,  $\text{R}_1$ ,  $\text{R}_3$ ,  $\text{R}_4$ ,  $\text{R}_5$ ,  $\text{R}_8$ ,  $\text{R}_9$ ,  $\text{R}_{10}$  and  $\text{R}_{11}$ , each represents an aryl or substituted aryl group (e.g. phenyl, tolyl, hydroxyphenyl, carboxyphenyl, aminophenyl or mercaptophenyl, carboxyethyl, nitrophenyl, ethoxyphenyl, iodophenyl, methoxyphenyl, cyanophenyl, acetamidophenyl,  $\alpha$ -naphthyl,  $\beta$ -naphthyl, hydroxynaphthyl, carboxynaphthyl or aminonaphthyl); or a heterocyclic group selected from fur-2-yl, thien-2-yl, quinol-2-yl, benzoxyazol-2-yl, thiadiazolyl, benzothiadiazolyl, oxazolyl, pyrimidinyl, pyridyl, and 2,5-dimethyl-thiazolyl. The group can advantageously contain an electron-sharing group capable of forming a metal chelate or a complex, such as primary, secondary, tertiary amido oxime, thio ether, keto, thioketo, hydroxyl, mercapto, carboxyl, sulfo, phospho or alkoxyl,  $\text{R}_2$ ,  $\text{R}_6$  and  $\text{R}_7$ , each represent a group selected from an aryl or substituted aryl group (such as a phenyl group or naphthyl group), a heterocyclic group (as defined for  $\text{R}$ , etc.), an allyl or substituted alkyl group (e.g. methyl, ethyl, propyl, butyl, mercaptomethyl or mercaptoethyl or a carboxyalkyl group such as methoxycarbonyl or ethoxycarbonyl), hydroxyl, carboxyl or a salt thereof, an amino group (e.g. amino, ethylamino or anilino), mercapto, cyano, acyl, nitro or hydrogen.  $\text{D}$  represents a divalent aromatic group;  $\text{E}$  represents alkylene, arylene or aralkylene.  $\text{X}$  is an anion; and  $n$  is 1 or 2, provided that the compound forms an intramolecular salt when  $n$  is 1.

In the above formula; the divalent aromatic group for  $\text{E}$  is preferably an arylene group (e.g. phenylene, alkoxy-substituted phenylene such as methoxy-substituted phenylene, naphthylene or diphenylene), or a divalent aromatic heterocyclic group.

The following are typical examples of the cationic moieties of the tetrazolium compounds represented by the formula but not intended to limit the tetrazolium compound thereof.

- (1) 2 - (Benzothiazol - 2 - yl) - 3 - phenyl - 5 - dodecyl - 2H - tetrazolium
- (2) 2,3 - Diphenyl - 5 - (4 - t - octyloxyphenyl) - 2H - tetrazolium
- (3) 2,3,5-Triphenyl-2H-tetrazolium
- (4) 2,3,5 - Tri(p-carboxyethylphenyl)-2H-tetrazolium
- (5) 2-(Benzothiazol-2-yl) - 3 - phenyl - 5 - (o - chlorophenyl) - 2H - tetrazolium
- (6) 2,3-Diphenyl-2H-tetrazolium
- (7) 2,3-Diphenyl-5-methyl-2H-tetrazolium
- (8) 3 - (p - Hydroxyphenyl) - 5 - methyl - 2 - phenyl - 2H - tetrazolium
- (9) 2,3-Diphenyl-5-ethyl-2H-tetrazolium
- (10) 2,3-Diphenyl-5-n-hexyl-2H-tetrazolium
- (11) 5-Cyano-2,3-diphenyl-2H-tetrazolium
- (12) 2 - (Benzothiazol - 2 - yl) - 5 - phenyl - 3 - (4 - tolyl) - 2H - tetrazolium
- (13) 2 - (Benzothiazol - 2 - yl) - 5 - (4 - chlorophenyl - 3 - (4 - nitrophenyl) - 2H - tetrazolium

	(14) 5 - Ethoxycarbonyl - 2,3 - di(3 - nitrophenyl) - 2H - tetrazolium	
	(15) 5 - Acetyl - 2,3 - di(p - ethoxyphenyl) - 2H - tetrazolium	
	(16) 2,5 - Diphenyl - 3 - (p - tolyl) - 2H - tetrazolium	
	(17) 2,5 - Diphenyl - 3 - (p - iodophenyl) - 2H - tetrazolium	
5	(18) 2,3 - Diphenyl - 5 - (p - diphenyl) - 2H - tetrazolium	5
	(19) 5 - (p - Bromophenyl) - 2 - phenyl - 3 - (2,4,6 - trichlorophenyl) - 2H - tetrazolium	
	(20) 3 - (p - Hydroxyphenyl) - 5 - (p - nitrophenyl) - 2 - phenyl - 2H - tetrazolium	
10	(21) 5 - (3,4 - Dimethoxyphenyl) - 3 - (2 - ethoxyphenyl) - 2 - (4 - methoxy - phenyl) - 2H - tetrazolium	10
	(22) 5 - (4 - Cyanophenyl) - 2,3 - diphenyl - 2H - tetrazolium	
	(23) 3 - (p - Acetamidophenyl) - 2,5 - diphenyl - 2H - tetrazolium	
	(24) 5-Acetyl-2,3-diphenyl-2H-tetrazolium	
15	(25) 5-(Fur-2-yl)-2,3-diphenyl-2H-tetrazolium	15
	(26) 5-(Thien-2-yl)-2,3-diphenyl-2H-tetrazolium	
	(27) 2,3-Diphenyl-5-(pyrid-4-yl)-2H-tetrazolium	
	(28) 2,3-Diphenyl-5-(quinol-2-yl)-2H-tetrazolium	
	(29) 2,3-Diphenyl-5-(benzoxazol-2-yl)-2H-tetrazolium	
20	(30) 2,4-Diphenyl-5-nitro-2H-tetrazolium	20
	(31) 2,2',3,3' - Tetraphenyl - 5,5' - 1,4 - butylene - di - (2H - tetrazolium)	
	(32) 2,2',3,3' - Tetraphenyl - 5,5' - p - phenylene - di - (2H - tetrazolium)	
	(33) 2 - (4,5 - Dimethylthiazol - 2 - yl) - 3,5 - diphenyl - 2H - tetrazolium	
	(34) 3,5 - Diphenyl - 2 - (triazin - 2 - yl) - 2H - tetrazolium	
25	(35) 2 - (Benzothiazol - 2 - yl) - 3 - (4 - methoxyphenyl) - 5 - phenyl - 2H - tetrazolium	25
	(36) 2,5 - diphenyl - 3 - $\alpha$ - naphthyl - 2H - tetrazolium	
	(37) 3,3' - (3,3' - dimethoxy - 4,4' - diphenylene) - 2,2',5,5' - tetraphenyl - di - (2H - tetrazolium)	
30	The anion X can be a halogen ion, a thiosulfate anion, a sulfate anion, a thiocyanate anion, an alkylsulfate anion, a nitrate anion, an acetate anion, a lower alkylbenzene sulfonate anion for the diffusible tetrazolium compound and a higher alkylbenzenesulfonate anion such as p-dodecylbenzenesulfonate anion, a higher alkylsulfate anion such as laurylsulfate anion, a dialkyl sulfo succinate anion such as di - 2 - ethylhexylsulfo succinate anion, a polyether alcohol sulfate anion such as cetyl polyethenoxy sulfate anion, a higher fatty acid anion such as stearic acid anion, or a polymer having acid radicals such as polyacrylate anion for the non-diffusible tetrazolium compound.	30
35	Most typical examples of the compounds of the invention are as follows:	35
40	[1] Diffusible tetrazolium compounds:	40
	(1) 2,3,5-Triphenyl-2H-tetrazolium chloride	
	(2) 2,3,5 - Tri(p - carboxyethylphenyl) - 2H - tetrazolium iodide	
	(3) 2-(Benzothiazol - 2 - yl) - 3 - phenyl - 5 - (o - chlorophenyl) - 2H - tetrazolium bromide	
45	(4) 2,3-Diphenyl-2H-tetrazolium thiasulfate	45
	(5) 2,3 - Diphenyl - 5 - methyl - 2H - tetrazolium chloride	
	(6) 3 - (p - Hydroxyphenyl) - 5 - methyl - 2 - phenyl - 2H - tetrazolium sulfate	
	(7) 2,3 - Diphenyl - 5 - ethyl - 2H - tetrazolium chloride	
	(8) 2,3 - Diphenyl - 5 - n - hexyl - 2H - tetrazolium chloride	
50	(9) 5 - Cyano - 2,3 - diphenyl - 2H - tetrazolium thiocyanate	50
	(10) 2 - (Benzothiazol - 2 - yl) - 5 - phenyl - 3 - (4 - tolyl) - 2H - tetrazolium chloride	
	(11) 2 - (Benzothiazol - 2 - yl) - 5 - (4 - chlorophenyl) - 3 - (4 - nitrophenyl) - 2H - tetrazolium chloride	
55	(12) 5 - Ethoxycarbonyl - 2,3 - di(3 - nitrophenyl) - 2H - tetrazolium bromide	55
	(13) 5 - Acetyl - 2,3 - di(p - ethoxyphenyl) - 2H - tetrazolium chloride	
	(14) 2,5 - Diphenyl - 3 - (p - tolyl) - 2H - tetrazolium methylsulfate	
	(15) 2,5 - Diphenyl - 3 - (p - iodophenyl) - 2H - tetrazolium chloride	
	(16) 2,3 - Diphenyl - 5 - (p - diphenyl) - 2H - tetrazolium chloride	
60	(17) 5 - (p - Bromophenyl) - 2 - phenyl - 3 - (2,4,6 - trichlorophenyl) - 2H - tetrazolium chloride	60

	(18) 3 - (p - Hydroxyphenyl) - 5 - methyl - 2 - phenyl - 2H - tetrazolium chloride	
	(19) 5 - (3,4 - Dimethoxyphenyl) - 3 - (2 - ethoxyphenyl) - 2 - (4 - methoxyphenyl) - 2H - tetrazolium chloride	
5	(20) 5 - (4 - Cyanophenyl) - 2,3 - diphenyl - 2H - tetrazolium chloride	5
	(21) 3 - (p - Acetamidophenyl) - 2,5 - diphenyl - 2H - tetrazolium chloride	
	(22) 5 - Acetyl - 2,3 - diphenyl - 2H - tetrazolium chloride	
	(23) 5 - (Fur - 2 - yl) - 2,3 - diphenyl - 2H - tetrazolium chloride	
	(24) 5 - (Thien - 2 - yl) - 2,3 - diphenyl - 2H - tetrazolium chloride	
10	(25) 2,3 - Diphenyl - 5 - (pyrid - 4 - yl) - 2H - tetrazolium nitrate	10
	(26) 2,3 - Diphenyl - 5 - (quinol - 2 - yl) - 2H - tetrazolium chloride	
	(27) 2,3 - Diphenyl - 5 - (benzoxazol - 2 - yl) - 2H - tetrazolium chloride	
	(28) 2,3 - Diphenyl - 5 - nitro - 2H - tetrazolium methylsulfate	
15	(29) 2,2',3,3' - Tetraphenyl - 5,5' - 1,4 - butylene - di - (2H - tetrazolium chloride)	15
	(30) 2,2',3,3' - Tetraphenyl - 5 - 5' - p - phenylene - di - (2H - tetrazolium chloride)	
	(31) 2 - (4,5 - Dimethylthiazol - 2 - yl) - 3,5 - diphenyl - 2H - tetrazolium chloride	
20	(32) 3,5 - Diphenyl - 2 - (triazin - 2 - yl) - 2H - tetrazolium sulfate	20
	(33) 2 - (Benzothiazol - 2 - yl) - 3 - (4 - methoxyphenyl) - 5 - phenyl - 2H - tetrazolium chloride	
	(34) 2,5 - diphenyl - 3 - $\alpha$ - naphthyl - 2H - tetrazolium chloride	
25	(35) 3,3' - (3,3' - dimethoxy - 4,4' - diphenylene) - 2,2',5,5' - tetraphenyl - di - (2H - tetrazolium chloride)	25
	(36) 5 - (3 - methoxyphenyl) - 3 - (3 - trifluoromethylphenyl) - 2 - phenyl - 2H - tetrazolium acetate.	

[2] Non diffusible tetrazolium compounds:

30	(37) 2 - (Benzothiazol - 2 - yl) - 3 - phenyl - 5 - dodecyl - 2H - tetrazolium bromide	30
	(38) 2,3 - Diphenyl - 5 - (4 - t - octyloxyphenyl) - 2H - tetrazolium chloride	
	(39) 2,3,5 - Triphenyl - 2H - tetrazolium diethylhexylsuccinate sulfonate	
	(40) 2,3,5 - Tri(p - carboxyethylphenyl) - 2H - tetrazolium p - dodecylbenzene - sulfonate.	
35	(41) 2 - (Benzothiazol - 2 - yl) - 3 - phenyl - 5 - (o - chlorophenyl) - 2H - tetrazolium diethylhexylsuccinate sulfonate	35
	(42) 2,3 - Diphenyl - 2H - tetrazolium p - octylbenzenesulfonate	
	(43) 2,3 - Diphenyl - 5 - methyl - 2H - tetrazolium laurylsulfate	
40	(44) 3 - (p - Hydroxyphenyl) - 5 - methyl - 2 - phenyl - 2H - tetrazolium isopropyl-naphthalenesulfonate	40
	(45) 2,3 - Diphenyl - 5 - ethyl - 2H - tetrazolium di - ethylhexylsulfosuccinate	
	(46) 2,3 - Diphenyl - 5 - n - hexyl - 2H - tetrazolium cetyl-polyethenoxysulfate	
	(47) 5 - Cyano - 2,3 - diphenyl - 2H - tetrazolium polyacrylate	
45	(48) 2 - (Benzothiazol - 2 - yl) - 5 - phenyl - 3 - (4 - tolyl) - 2H - tetrazolium diethylhexylsuccinate sulfonate	45
	(49) 2 - (Benzothiazol - 2 - yl) - 5 - (4 - chlorophenyl) - 3 - (4 - nitrophenyl) - 2H - tetrazolium diethylhexylsuccinate sulfonate	
	(50) 5 - Ethoxycarbonyl - 2,3 - di(3 - nitrophenyl) - 2H - tetrazolium-diethylhexylsuccinate sulfonate	
50	(51) 5 - Acetyl - 2,3 - di(p - ethoxyphenyl) - 2H - tetrazolium-diethylhexylsuccinate sulfonate	50
	(52) 2,5 - Diphenyl - 3 - (p - tolyl) - 2H - tetrazolium - p - octylbenzenesulfonate	
55	(53) 2,5 - Diphenyl - 3 - (p - iodophenyl) - 2H - tetrazolium - p - octylbenzenesulfonate	55
	(54) 2,3 - Diphenyl - 5 - (p - diphenyl) - 2H - tetrazolium - p - octylbenzenesulfonate	
	(55) 5 - (p - Bromophenyl) - 2 - phenyl - 3 - (2,4,6 - trichlorophenyl) - 2H - tetrazolium isopropyl-naphthalenesulfonate	
60	(56) 3 - (p - Hydroxyphenyl) - 5 - (p - nitrophenyl) - 2 - phenyl - 2H - tetrazolium diethylhexylsuccinate sulfonate	60
	(57) 5 - (3,4 - Dimethoxyphenyl) - 3 - (2 - ethoxyphenyl) - 2 - (4 - methoxyphenyl) - 2H - tetrazolium diethylhexylsuccinate sulfonate	

	(58) 5 - (4 - Cyanophenyl) - 2,3 - diphenyl - 2H - tetrazolium diethylhexylsuccinate sulfonate	
	(59) 3 - (p - Acetamidophenyl) - 2,5 - diphenyl - 2H - tetrazolium laurylsulfate	
5	(60) 5 - Acetyl - 2,3 - diphenyl - 2H - tetrazolium diethylhexylsuccinate sulfonate	5
	(61) 5 - (Fur - 2 - yl) - 2,3 - diphenyl - 2H - tetrazolium diethylhexylsuccinate sulfonate	
	(62) 5 - (Thien - 2 - yl) - 2,3 - diphenyl - 2H - tetrazolium diethylhexylsuccinate sulfonate	
10	(63) 2,3 - Diphenyl - 5 - (pyrid - 4 - yl) - 2H - tetrazolium diethylhexylsuccinate sulfonate	10
	(64) 2,3 - Diphenyl - 5 - (quinol - 2 - yl) - 2H - tetrazolium diethylhexylsuccinate sulfonate	
15	(65) 2,3 - Diphenyl - 5 - (benzoxazol - 2 - yl) - 2H - tetrazolium diethylhexylsuccinate sulfonate	15
	(66) 2,4 - Diphenyl - 5 - nitro - 2H - tetrazolium polyacrylate	
	(67) 2,2',3,3' - Tetraphenyl - 5,5' - 1,4 - butylene - di - (2H - tetrazolium) laurylsulfate	
20	(68) 2,2',3,3' - Tetraphenyl - 5,5' - p - phenylene - di - (2H - tetrazolium) cetyl-polyethenoxysulfate	20
	(69) 2 - (4,5 - Dimethylthiazol - 2 - yl) - 3,5 - diphenyl - 2H - tetrazolium polyacrylate	
	(70) 3,5 - Diphenyl - 2 - (triazin - 2 - yl) - 2H - tetrazolium stearate	
25	(71) 2 - (Benzothiazol - 2 - yl) - 3 - (4 - methoxyphenyl) - 5 - phenyl - 2H - tetrazolium di - ethylhexylsulfosuccinate	25
	(72) 2,5 - Diphenyl - 3 - $\alpha$ - naphthyl - 2H - tetrazolium dodecylsulfate	
	(73) 3,3' - (3,3' - Dimethoxy - 4,4' - diphenylene) - 2,2',5,5' - tetraphenyl - di - (2H - tetrazolium) polyacrylate	
30	(74) 5 - (3 - Methoxyphenyl) - 3 - (3 - trifluoromethylphenyl) - 2 - phenyl - tetrazolium isopropyl-naphthalenesulfonate	30

35 The non-diffusible or diffusible tetrazolium compounds according to the invention are thus synthesized by an optional selection of the anionic and cationic moiety. The non-diffusible compounds, e.g. 2,3,5 - triphenyl - 2H - tetrazolium dioctyl - succinate - sulfonate, may be dispersed into a gelatin solution by mixing a corresponding soluble tetrazolium salt with the gelatin solution and then an anion that will provide a non-diffusible tetrazolium compound is admixed thereto, thereby to obtain the gelatin solution with a dispersed non-diffusible tetrazolium compound as specifically mentioned in Examples set forth later.

40 Alternatively, crystals of the non-diffusible tetrazolium compound synthesized as such may be dissolved in a suitable solvent, such as dimethylsulfoxide, and then dispersed in the gelatin solution. When the dispersion is not sufficiently homogeneous, good results may be obtained by exposing the emulsion dispersion to ultrasonic waves, or by use of a suitable homogenizer such as Manton-Gaulin homogenizer.

45 As mentioned above, the tetrazolium compounds of this invention may be used both in diffusible and non-diffusible forms, when the silver halide of this invention is employed. However, the higher contrast image may be obtained by employing the non-diffusible tetrazolium compounds. Accordingly, it is advantageous to employ the non-diffusible tetrazolium compound when an especially superior dot quality is required.

50 On the other hand, the use of too much high contrast light-sensitive material sometimes brings about not sufficient reproduction of the line image, particularly those of fine letters and lines. In this case an image with more superior quality may be obtained by the use of the diffusible tetrazolium compounds.

55 According to a preferred embodiment of the invention, the tetrazolium compound of the invention is incorporated into a silver halide emulsion layer.

According to another preferred embodiment of the invention, the compound is incorporated in a layer adjacent (or a layer adjacent to said adjacent layer) to the layer containing the silver halide emulsion.

60 The above-mentioned tetrazolium compounds used according to the invention may preferably be employed in an amount of 0.0001 — 10 mole, more preferably 0.001 — 1 mole, per mole of the silver halide contained in the light-sensitive silver halide photographic material of the invention. As the silver halide employed for the light-sensitive silver halide photographic material of the invention includes any

silver chlorobromide or silver chloriodobromide containing at least 50 mole % of silver chloride, and having an average grain size of 0.1 — 0.5  $\mu$ , and at least 80% of the total grains being within a range of 0.7 — 1.3 times the average grain size.

The silver halide emulsion used according to the invention may be sensitized with various kinds of chemical sensitizers. As the sensitizers, are mentioned, for example, activated gelatin, sulfur sensitizers (e.g. sodium thiosulfate aryl thiocarbamide, thiourea or aryl isocyanate) selenium sensitizers (e.g. N,N-dimethylselenourea or selenourea, etc). reducing sensitizers (e.g. triethylene-tetramine or stannic chloride), and various noble metal sensitizers represented by potassium chloraurite, potassium auriothiocyanate, potassium chloraurate, 2-auro-sulfobenzothiazole methylchloride, ammonium chloropalladate, potassium chloroplatinate and sodium chloropalladite. The sensitizer may be employed alone, or mixed together. Ammonium thiocyanate may be auxiliarily employed when a gold sensitizer is employed.

Furthermore, the silver halide emulsion used in the invention may be sensitized optically with one or more sensitizing dyes to give a light sensitivity within the desired light-sensitive wave length.

Various kinds of sensitizing dyes may be employed for the purpose. Our co-pending British Patent Application No. 31451/77 (Serial No. 1 589 584) describes and claims photographic materials containing such dyes and otherwise similar to those of this invention. As the optical sensitizers employed advantageously in the invention are mentioned, e.g. a cyanine, merocyanine, tri- or tetranuclei merocyanine, tri- or tetranuclei cyanine, hemicyanine, oxonole, and hemioxonole.

The optical sensitizers preferably contain within the chemical structure thereof a nitrogen-containing heterocyclic nucleus, e.g. a basic group such as thiazoline of thiazole, or rhodanine, thiohydantoin, oxazolidine-dione, barbituric acid, thiobarbituric acid or pyrazolone. The nucleus may be substituted with an alkyl, hydroxyalkyl, halogen, phenyl, cyano or alkoxy group or may be fused with a hydrocarbon or heterocyclic ring.

The silver halide emulsion of the invention may preferably be stabilized with 5,6 - trimethylene - 7 - hydroxy - s - triazole(1,5 - a)pyrimidine, 5,6 - tetramethylene - 7 - hydroxy - s - triazolo(1,5 - a)pyrimidine, 5 - methyl - 7 - hydroxy - s - triazolo(1,5 - a)pyrimidine, 7 - hydroxy - s - triazolo(1,5 - a)pyrimidine, 5 - methyl - 6 - bromo - 7 - hydroxy - s - triazolo(1,5 - a)pyrimidine, esters or salts of gallic acid (e.g. isoamyl gallate, dodecyl gallate, propyl gallate or sodium gallate), mercaptans (e.g. 1 - phenyl - 5 - mercaptotetrazole or 2 - mercaptobenzothiazole), benzotriazoles (e.g. 5 - bromobenzotriazole or 4 - methylbenzotriazole) and benzimidazoles (e.g. 6-nitrobenzimidazole). Such stabilizers are described in, e.g. U.S. Patents 2,444,607, 2,716,062, 3,512,982, 3,342,596, 3,726,686 and 3,717,465, British Patent 1,363,921. Furthermore the silver halide emulsion of the invention may contain a latent image stabilizer such as a sulfur-containing amino acid, or a gradation-adjusting agent such as a cadmium or rhodium salt, described in, e.g. British Patent 1,343,904 and U.S. Patent 3,821,295.

It has been known in, e.g. British Patent 775,197 and U.S. Patent 3,488,709, to employ a rhodium or cadmium salt to increase the contrast of silver halide emulsion. However, problems still remain when the rhodium salt is employed. For example, the use of rhodium salt tends to cause an unevenness of the product due to the minute amount of addition and the narrow allowable range thereof of the salt, and thus makes it difficult to produce stable photographic materials. In case of the cadmium salt, it has to be added as little as possible from an ecological viewpoint, for it is washed out by film-processing and comes finally into the environment. The cadmium salts are known to prevent the metabolism and to be harmful to living tissues. Cadmium may be detected not only in air but also in the body of sea animals. As a result of interest in public health and in the maintenance of normal ecological balance in view of the toxicity of rare metals, including cadmium mentioned above, the inventors have reached the invention relating to a novel method to obtain a light-sensitive material with sufficiently high contrast, even with no use of such harmful metals. When the above-mentioned silver halide and tetrazolium compound of the invention are incorporated into the hydrophilic colloidal layer.

The hydrophilic colloid advantageously employed in the invention is gelatin. As other hydrophilic colloids than gelatin are mentioned, e.g. colloidal albumin, agar, gum arabic, arginic acid, hydrolyzed cellulose acetate, acrylamide, imidated polyamide, polyvinyl alcohol, hydrolyzed polyvinyl acetate, water-soluble polymer

described in, e.g. British Patent 523,661, U.S. Patents 3,847,620, 3,655,389 and 3,341,332, gelatin derivatives such as phenylcarbamyl-acylated- or phthalated-gelatin described in, e.g. U.S. Patents 2,614,928 and 2,525,753, or graft-polymerized monomers on gelatin having the ethylene group and being capable of polymerization, such as acrylic acid and the ester thereof, styrene, methacrylic acid and the ester thereof, described in e.g. U.S. Patents 2,548,520 and 2,831,767. Such hydrophilic colloids may also be applied to a layer containing no silver halide, e.g. an antihalation layer, a protective layer or an intermediate layer.

The light-sensitive silver halide material of the invention may be prepared by coating the above-mentioned layer containing the silver halide and the tetrazolium compound of the invention on a suitable photographic base. As the representative supports employed in the invention are mentioned, e.g. baryta paper, a polyethylene-coated paper, a synthetic polypropylene paper, a glass plate, a cellulose acetate or cellulose nitrate film, a polyester film such as a polyethylene terephthalate film, a polyamide film, a polypropylene film, a polycarbonate film, or a polystyrene film. The supports are optionally selected depending on the purpose for which the light-sensitive photographic material is used.

As mentioned above, the light-sensitive silver halide photographic material of the invention comprises at least one hydrophilic colloidal layer, coated on the support, containing a silver halide of this invention and the tetrazolium compound of the invention.

It is preferable in the light-sensitive material of the invention that a protective layer having a suitable thickness is coated. The protective layer is advantageously a gelatin layer, the thickness of which is preferably 0.1 — 10  $\mu$ , more preferably 0.8 — 2.0  $\mu$ .

The hitherto known lith type light-sensitive silver halide photographic materials usually have a protective layer. In this invention, however, the protective layer plays an important role different from known ones.

The protective layer is, in general, provided to protect the silver halide emulsion layer from incidental mechanical damage during production processes, e.g. cutting, winding or wrapping process, or during photographing and/or processing caused by contact of the light-sensitive material with other substance.

It has turned out that the protective layer of the invention not only protects the above-mentioned silver halide emulsion but also plays an important role for processing stability. That is, while the lith type light-sensitive material has to be able to form a very high contrast line- and dot-image, if a compound oxidizable by a hydroquinone developing agent is added in the light-sensitive silver halide photographic material to obtain the above-mentioned high contrast silver image, the above-mentioned oxidizing agent gives a large influence on the development during the progress thereof and consequently, the quality of the line- or dot-image obtained is largely influenced by the difference of e.g. developing time, temperature and amount of the exposure.

It is not necessarily elucidated in the process of the invention why the presence of the protective layer may act effectively on the stability of the image quality and of the developing process. Presumably, the protective layer may have a function to control adequately the infiltration rate of the hydroquinone/Metol or 1 - phenyl - 3 - pyrazolidone from the processing solution into the light-sensitive material, or the diffusion rate of the tetrazolium compound within the light sensitive material or therefrom to the processing solution.

This effect is remarkable when the tetrazolium compound is employed according to the invention. The effect is not so remarkable when other oxidizing agents than the tetrazolium compound described in, e.g. Japanese Patent Provisional Publication No. 52—18317 (1977) are employed.

Various kinds of photographic additives may optionally be added to the above-mentioned hydrophilic colloid of the invention, as far as they do not impair the effect of the invention. As the additives, are mentioned, e.g. a gelatin plasticizer, a hardening agent, a surface active agent, an image stabilizer, an ultraviolet absorber, an antistaining agent, a pH adjuster, an antioxidant, an antistatic agent, a viscosity-increasing agent, a granularity improving agent, a dye, a mordant, a brightening agent, a development regulator, or a matting agent.

Among the additives mentioned above, the following may particularly and preferably be employed: viscosity-increasing agents and plasticizers, described in U.S. Patents 2,960,404, 3,767,410, 3,659,956 and 3,692,753, e.g. a styrene/sodium maleate copolymer and dextran sulfate, etc; hardening agents of an aldehyde, epoxy, ethyleneimine, active halogen, vinylsulfone, isocyanate, sulfinic acid ester,



carbodiimide, a mucochloric acid, or acyloyls; image stabilizers, e.g. 6,6' - butylidene - bis(2 - t - butyl - 4 - methyphenol) and 4,4' - methylene - bis(2,6 - di - t - butylphenol); ultraviolet absorbers, described in e.g. U.S. Patent 3,253,921, British Patent 1,309,349, U.S. Patents 3,533,794 and 3,707,375 and British Patent 1,287,770, particularly 2 - (2 - hydroxy - 5 - t - butylphenyl) - benzotriazole, 2 - (2 - hydroxy - 3,5 - di - t - butylphenyl)benzotriazole, 2 - (2 - hydroxy - 3 - t - butyl - 5 - butylphenyl - 5 - chlorobenzotriazole and 2 - (hydroxy - 3,5 - di - t - butylphenyl) - 5 - chlorobenzotriazole; surface active agents for coating aids; emulsifiers, infiltration-improving agents for a processing solution, defoamers, or agents for controlling various physical properties of the light-sensitive material, described in, e.g. U.S. Patents 3,026,202 and 3,514,293, British Patents 548,532 and 1,216,389, U.S. Patent 3,726,683, including anionic, cationic, nonionic and amphoteric compounds; mordants described in, e.g. U.S. Patents 2,113,381 and 2,548,564; antistaining agents described in, e.g. U.S. Patents 2,360,210, 2,728,659, 2,732,300 and 3,700,453, particularly 2 - methyl - 5 - hexadecylhydroquinone, 2 - methyl - 5 - sec - octadecylhydroquinone and 2,5 - di - t - octylhydroquinone; antistatic agents described in, e.g. U.S. Patents 2,882,157, 2,972,535, and 3,573,093 and British Patent 1,378,584 and U.S. Patents 3,549,369, 3,704,128 and 3,663,230; matting agents described in, e.g. U.S. Patents 2,992,101 and 2,956,884, British Patents 1,221,980 and 1,307,373, particularly silica gel having a grain size of 0.5 — 20  $\mu$  and polymethylmethacrylate having a grain size of 0.5 — 20 $\mu$ ; developing promoters, e.g. benzyl alcohol and a polyoxyethylene series compound which may be added in the processing bath.

In accordance with the process of the invention, there is obtained a high contrast silver image. The invention is therefore applicable to various fields wherein a high contrast black and white recording is required. The light-sensitive material of the invention is, for example, applied preferably to a printing- or micro-sensitive material.

The process of the invention for forming a lith type photographic image has superior characteristics which no conventional processes have reached yet.

It is not completely certain why the high contrast silver image may be obtained according to the process of the invention. It is presumed that the semiquinone produced by oxidation of hydroquinone in the developing solution by the tetrazolium compound may be accumulated in an abnormally high concentration near the developed silver.

It is said, in general, that the so-called "infectious phenomenon" does not take place due to instantaneous removal of the semiquinone or quinones by sulfonation when the sulfite ions are in a high concentration in the developing solution. Whereas in the present process, it is presumed as if the infectious development takes place at the position of the exposed silver halide in the gelatin layer due to predominant supply of the semiquinone.

It is accordingly essential in the process of the invention to treat with a developing solution containing a hydroquinone developing agent. The lith type developing solution (infectious developing solution), however, it is not essentially required as far as the solution is of hydroquinones, by which high contrast lith type silver image may sufficiently be obtained even in the presence of sulfite ion in a high concentration.

The process of the invention differs apparently from the conventional processes in that no conventional lith type developing solution which contains hydroquinone, alkali, alkali metal bromide, sulfite ion in low concentration, and as a preservative a condensation product of formaldehyde/sodium bisulfite or carbonylbisulfite amine is needed, although the use of such components may of course be possible.

As the hydroquinone type developing agents employed in the invention are mentioned, e.g. hydroquinone, chlorohydroquinone, bromohydroquinone, isopropylhydroquinone, toluhydroquinone, methylhydroquinone, 2,3-dichlorohydroquinone, 2,5-dimethylhydroquinone, 2,3-dibromohydroquinone, 2,5 - dihydroxyacetophone, 2,5 - diethylhydroquinone, 2,5 - di - p - phenethylhydroquinone, and 2,5 - dibenzoylaminoquinone.

The developing solution containing the hydroquinones developing agent employed in the invention includes not only the so-called lith type developing agent but also the gradient MQ and PQ developing solution, the latter of which are advantageously employed in the invention because of the easiness of preparation and superior preservability. Among these developing solutions, those which show the superadditivity are preferred. For example, the developing agents and the

additives therefor described in "The Theory of Photographic Process," Third Edition, pp 374—378 (1966) are advantageously employed. A preserver like sulfite salts such as sodium sulfite, potassium sulfite or ammonium sulfite may jointly be employed in the developing solution used in the invention without impairing the effect of the invention; and this is another characteristic of the invention. The adjustment of pH and giving a buffer function with an alkali hydroxide, alkali carbonate or amine, or addition of inorganic development retarder such as potassium bromide or of organic development retarder such as benzotriazole may optionally be carried out as in the standard black and white developing solution.

In the invention the phrase "treat with a developing solution containing hydroquinones developing agent" means to carry out development of the exposed material of the invention with the developing solution which satisfies the above-mentioned conditions, and various modes may be included therein. For example, the temperature at which development is carried out is preferably below 50°C, more preferably around 30°C, and the time required for development is generally within 30 minutes, more preferably within 5 minutes, by which good results are obtained, in general.

After the development, the subsequent processes such as washing, stopping, stabilizing and fixing are carried out. If necessary, processes like prehardening and neutralization and the like may be adopted, but they may optionally be omitted. The processes may be carried out either by the so-called manual treatment like a bath- or tray-development or by the mechanical treatment like a roller- or hanger-development. According to a preferred embodiment of the invention, the processing solution in the bath development was more than 20 times stabler over long period than the conventional lith type developing solution. Especially, when the known particular developing solution containing sulfite ion in an extremely low concentration is employed in order to improve the dot quality of the lith type light-sensitive material, it became of no use for several hours. While, according to a preferred method of the invention, the processing solution could be stably employed after one month has passed, and the dot quality using the solution was then comparable to that using a newly prepared solution.

Furthermore, addition of a contrast agent often used for the conventional high contrast developing solution to the developing solution employed in the invention gives no undesirable influence on the photographic quality.

As can be clearly understood by the explanations given above, the invention relates to a novel light-sensitive silver halide photographic material and the processing method thereof which may obtain a superior line- or dot-image by processing the light-sensitive silver halide photographic material comprising a tetrazolium salt and a silver halide having a narrow grain size distribution, with a developing solution containing hydroquinone, using no infectious developing solution.

According to the process of the invention, there is obtained a high contrast silver image even when the diffusible tetrazolium compound is employed. There may also be obtained a dot image which is superior to that obtained by the method described in Japanese Patent Provisional Publication No. 52—18317 (1977), when the non-diffusible tetrazolium compound is employed.

The invention is further concretely explained by the following Examples, which by no means restrict the scope of the invention:

#### COMPARISON 1.

A silver chloriodobromide-gelatin emulsion comprising silver halide of 80 mole % chloride, 19 mole % bromide and 1 mole % iodide, having an average grain size of 0.3  $\mu$  and of 80 % grains within a range of 0.26 — 0.36  $\mu$  was sensitized chemically with sulfur- and gold-sensitizers. To the emulsion were added polyethyleneglycol (m.w. = 1540) oleic acid ester in an amount of 200 mg per mole of silver, and further 4 - hydroxy - 6 - methyl - 1,3,3a,7 - tetraazaindene and spiro - bis(3,3 - dimethyl - 5,6 - dihydroxyindane) in amounts of 100 mg and 20 mg per mole of silver, respectively. The emulsion was coated on a polyethylene terephthalate support in such amounts that those of the silver and the gelatin were 55 mg and 50 mg per 100 cm<sup>2</sup>, respectively. Further, on the silver halide emulsion layer, was coated gelatin in an amount of 30 mg per 100 cm<sup>2</sup> as a protective layer. The above-mentioned elements were wedge-exposed with a tungsten lamp through a gray contact screen and then processed at 30°C according to the following processes:

Developing : 1.5 min.  
 Stop fixing : 2 min.  
 Washing : 5 min.  
 Drying.

5 The following compositions were employed in the processing bath:

5

[Developing solution]

Metol 3.5 g  
 Anhydrous sodium sulfite 60 g  
 Hydroquinone 9.0 g  
 Sodium carbonate 54 g  
 Potassium bromide 2.5 g  
 5-Nitrobenzimidazole 0.5 g  
 1-Phenyl-5-mercaptotetrazole 20 mg  
 Water to make 1 litre (pH = 10.25).

10

10

15

[Stop fixer]

15

Ammonium thiosulfate decahydrate 150 mg  
 Anhydrous sodium sulfite 10 g  
 Sodium acetate trihydrate 15 g  
 Glacial acetic acid 15 ml

20

Water to make 1 litre (ph = 4.20)

20

Comparison 2.

Comparison 1 was repeated, except that potassium dichromate was added, in advance of coating, to the emulsion in an amount of 4 g per mole of silver.

Comparison 3.

25

Comparison 1 was repeated, except that potassium persulfate was added, in advance of coating, to the emulsion in an amount of 4.0 g per mole of silver instead of potassium dichromate used in Comparison 2.

25

Example 1.

30

A material was prepared in the similar manner as in Comparison 1, except that 2,3,5 - triphenyl - tetrazolium chloride (Compound (1)) was added in advance of coating, to the emulsion in an amount of 4.5 g per mole of silver instead of potassium dichloromate used in Comparison 2.

30

Example 2.

35

A material was prepared in the similar manner as in Comparison 1, except that 3 - (p - hydroxyphenyl) - 5 - methyl - 2 - phenyl - 2H - tetrazolium chloride (Compound (18)) was added, in advance of coating, to the emulsion in an amount of 4.0 g per mole of silver instead of potassium dichromate used in Comparison 2.

35

Example 3.

40

A material was prepared in the similar manner as in Comparison 1, except that 2,3 - diphenyl - 5 - ethyl - 2H - tetrazolium chloride (Compound (7)) was added.

40

in advance of coating, to the emulsion in an amount of 4.0 g per mole of silver instead of potassium dichromate used in Comparison 2.

#### Example 4.

A material was prepared in the similar manner as in Comparison 1, except that a non-diffusible tetrazolium compound (Compound (66)) synthesized from 2,3 - diphenyl - 5 - nitro - 2H - tetrazolium chloride and polyacrylic acid was added, in advance of coating, to the emulsion in an amount of 8 g per mole of silver instead of potassium dichromate used in Comparison 1.

The results of Comparisons 1 to 3, and Examples 1 to 4 are summarized in Table 1.

TABLE 1

Sample	Relative sensitivity	$\gamma$	Fog	Dot quality
Comparison 1	100	6.42	0.06	2.0
„ 2	91	6.74	0.04	2.5
„ 3	89	6.66	0.04	2.5
Example 1	80	10.22	0.04	3.5
„ 2	83	9.87	0.04	3.0
„ 3	85	10.03	0.04	3.5
„ 4	92	12.85	0.04	5.0

As clearly shown in Table 1, the material according to the invention increases contrast very effectively and have a dot quality superior to other known oxidizing agents even when processed with the MQ developing solution, and therefore, has superior properties for the lith type light-sensitive material for the line- and dot-image use. Here, the term "dot quality" means an evaluation value for the reproduction quality of the half tone image.

The "lith type" photographic element (exposed using a half tone image and developed) produces usually a part called "shadow dot" and a part called "highlight part."

The intermediate part which is between the two parts has various sizes. The term "dot quality" referred to herein means an evaluation value of a part called "50 % dot", i.e. the concentration at which 50 % is clear and 50 % is developed, and is expressed by a progressive scale. Namely "4" means to be excellent and "1" means to be extremely bad. It is not normally allowed that the 50% dot quality is less than "3".

It has turned out, among the above-mentioned materials according to the invention, the use of the diffusible tetrazolium salt (Examples 1, 2 and 3) produces an slightly lower  $\gamma$ -value and dot quality, but of a rather superior characteristic for the reproduction of the line image, as compared with the use of the non-diffusible tetrazolium salt (The characteristic of line image was estimated visually by the reproducibility of the Chinese character "UTSU.").

#### Comparison 4.

A silver chloroiodobromide/gelatin emulsion comprising silver halide of 50 mole % chloride, 49 mole % bromide and 1 mole % iodide, having an average grain size of 0.25  $\mu$  and 75 % grain within a range of 0.23 — 0.28  $\mu$  was sensitized chemically with sulfur- and gold-sensitizers. To the emulsion were added polyethyleneglycol (m.w. = 1420) oleic acid ester in an amount of 200 mg per mole of silver, and further 4 - hydroxy - 6 - methyl - 1,3,3a,7 - tetraazaindene in an amount of 300 mg per mole of silver. The emulsion was coated on a polyethylene tetraphthalate support in such amounts that those of the silver and the gelatin were 55 mg and 50 mg per 100 cm<sup>2</sup>, respectively.

Further, on the silver halide emulsion layer, was coated gelatin in an amount of 30 mg per 100 cm<sup>2</sup> as a protective layer. The above-mentioned material was wedge-exposed with a tungsten lamp through a gray contact screen and then processed at 30°C according to the following processes:

5	Developing	: 2 min.	5
	Stop fixing	: 2 min.	
	Washing	: 5 min.	
	Drying.		

The processing bath was composed as follows:

10	[Developing solution]		10
	Formaldehyde/sodium acid sulfite adduct	50 g	
	Hydroquinone	15 g	
	Boric acid	8 g	
	Anhydrous sodium sulfite	2 g	
15	Sodium carbonate monohydrate	85 g	15
	Potassium bromide	2.5 g	
	6-Nitroindazole	0.1 g	
	Water	to make 1 litre (pH = 10.00)	

20	The same composition as in Comparison 1 was employed for the fixing solution.	20
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#### Comparison 5.

Comparison 4 was repeated, except that hexaammine-cobalt chloride was added, in advance of coating, to the emulsion in an amount of 3 g per mole of silver and that the following processing bath composition was employed:

25	[Developing solution]		25
	Metol	3.5 g	
	Anhydrous sodium sulfite	40 g	
	Hydroquinone	9.0 g	
	Sodium carbonate monohydrate	54 g	
30	Potassium bromide	2.5 g	30
	6-Nitroindazole	0.1 g	
	Water	to make 1 litre (pH = 10.25).	

#### Comparison 6.

35	Comparison 5 was repeated, except that Chloramine T (tosylchloramide sodium) was added, in advance of coating, to the emulsion in an amount of 3 g per mole of silver instead of hexaamminecobalt chloride used in Comparison 5.	35
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#### Example 5.

Comparison 5 was repeated, except that 2,5 - diphenyl - 3 -  $\alpha$  - naphthyl-

tetrazolium chloride (compound (34)) was added, in advance of coating, to the emulsion in an amount of 4 g per mole of silver instead of hexaamminecobalt used in Comparison 5.

#### Example 6.

5 Comparison 5 was repeated, except that 3,3' - (3,3' - dimethoxy - 4,4' - diphenylene) - 2,2',5,5' - phenyltetra - di - (2H - tetrazolium chloride) (Compound (=35)) was added, in advance of coating, to the emulsion in an amount of 1 g per mole of silver instead of hexaamminecobalt used in Comparison 5.

#### Example 7.

10 Example 6 was repeated, except that sodium dibutylhexylsuccinate sulfonate was further added in an amount of 1 g per litre to the developing solution used in Comparison 5.

The results of Comparisons 4 to 6 and Examples 5 to 7 are summarized in Table 2.

TABLE 2

Sample	Relative Sensitivity	$\gamma$	Fog	Dot quality
Comparison 4	100	4.40	0.06	2.0
„ 5	93	5.97	0.08	2.5
„ 6	88	6.02	0.08	2.5
Example 5	82	7.97	0.08	3.5
„ 6	85	8.21	0.06	3.0
„ 7	85	8.73	0.06	3.5

20 As clearly shown in Table 2, a high contrast image with a good dot quality is obtained even when the tetrazolium salt, among substantially the diffusible oxidizing agents, is treated with the MQ developing solution.

#### Example 8.

25 To 100 ml of 10 % gelatin solution kept at 40°C was added 10 ml of 10% 2,3,5-triphenyltetrazolium chloride (hereinafter referred to as "T-Salt"). To the solution was further added in an amount of 1 g per litre to the developing solution used in under vigorous stirring. After cooling, the mixture was made into a noodle-like mass and washed with washing water until no chloride ion was detected. The mixture contained (Compound (39)) and was redissolved and finally made up to 200 ml with water. It was then coated on a polyethylene terephthalate support in an amount of about 2.0 mg per 100 cm<sup>2</sup>, based on the T-Salt. On the layer was coated a lith type silver chlorobromide emulsion comprising silver halide of 70 mole % silver chloride and 30 mole % silver bromide, and having an average grain size of 0.25  $\mu$ , and about 80% grains within a range of 0.19—0.31  $\mu$ , in such amounts that those of the silver and the gelatin were 55 mg and 50 mg per 100 cm<sup>2</sup>, respectively, to prepare Sample A. To the Sample A was coated gelatin with a thickness of 1.5  $\mu$  to prepare Sample B. After drying, Samples A and B were wedge-exposed with a tungsten lamp through a gray contact screen and then processed at 30°C according to the following processes:

Developing	: 1 min., 1.5 min., 2 min., 2.5 min.
Stopping	: 1 min.
Fixing	: 2 min.
Washing	: 5 min.

5

Drying.

5

The following compositions were employed as the processing solutions:

[Developing solution]

	Metol	3.5 g	
	Anhydrous sodium sulfite	40 g	
10	Hydroquinone	9.0 g	10
	Sodium carbonate monohydrate	50 g	
	Potassium bromide	2.5 g	
	5-Nitrobenzimidazole	0.5 g	
	1-Phenyl-5-mercaptotetrazole	10 mg	
15	Water	to make 1 litre (pH = 10.25)	15

[Fixing solution]

	Ammonium thiosulfate decahydrate	150 g	
	Anhydrous sodium sulfite	10 g	
	Anhydrous sodium phosphate	15 g	
20	Water	to make 1 litre (pH = 6.20).	20

The results of Example 8 are summarized in Table 3

TABLE 3

Sample	Development Time (min.)	Dot quality	Dot stability
Sample A	1	3.0	poor
„	1.5	3.5	good
„	2	3.0	poor
„	2.5	3.0	poor
Sample B	1	3.5	good
„	1.5	4.5	excellent
„	2	4.5	excellent
„	2.5	3.5	good

As shown in Table 3, Sample B having the binding upper layer shows less changes in dot quality and dot stability, depending on the change of the development time and possesses a little better dot quality, as compared with Sample A having no binding upper layer. Here, the term "dot stability" means a regularity of the dot quality from small dot at slightly exposed part to large dot at highly exposed part and is expressed as "excellent" if regular, and as "poor," if irregular, by a three stage evaluation.

#### Example 9.

A silver halide emulsion containing silver halide of 80 mole % chloride and 20 mole % bromide, having an average grain size of  $0.18 \mu$  and 75% grains within a range of  $0.11 - 0.25 \mu$  was chemically sensitized with a gold sensitizer and thiosulfate. Then, thereinto were added the following:

4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene	0.78 g
Saponin	2.5 g
Formaldehyde	0.5 g
2,3,5-triphenyl-2H-tetrazolium-di-isopropylnaphalene-disulfonate	1.2 g

The thus prepared emulsion, was coated on a polyethyleneterephthalate support in such amounts that those of the silver and the gelatin were respectively 40 mg per  $100 \text{ cm}^2$  and 22 mg per  $100 \text{ cm}^2$ .

Furthermore, gelatin was coated thereon as a protective layer in an amount of 10 mg per  $100 \text{ cm}^2$ .

The above-mentioned material was wedge-exposed with a tungsten lamp and then processed at  $30^\circ\text{C}$  according to the following processes:



Developing : 2 min.  
 Stop fixing : 2 min.  
 Washing : 5 min.  
 Drying

5 The processing bath was composed as follows:

5

[Developing solution]

	Metol	1.0 g	
	Anhydrous sodium bisulfite	75.0 g	
	Hydroquinone	9.0 g	
10	Sodium carbonate monohydrate	29.0 g	10
	Potassium bromide	4.0 g	
	Water	to make 1 litre (pH = 10.00)	

The same composition as in Comparison 1 was employed for the fixing solution.

15

Comparison 7.

15

The emulsion was prepared and processed in the same method as in Example 9 except that the silver halide was of 1.65  $\mu$  in an average grain size and the 25 % grains thereof were within a range of 1.0 — 2.3  $\mu$ .

The results of Comparison 7 and Example 9 are shown in Table 4.

TABLE 4

Sample	Relative Sensitivity	Fog	$\gamma$	Dot quality
Comparison 7	100	0.05	7.01	2.5
Example 9	75	0.04	11.72	4.0

As clear from the above, the sample of the invention is understood as excellently improved in dot quality and high contrast.

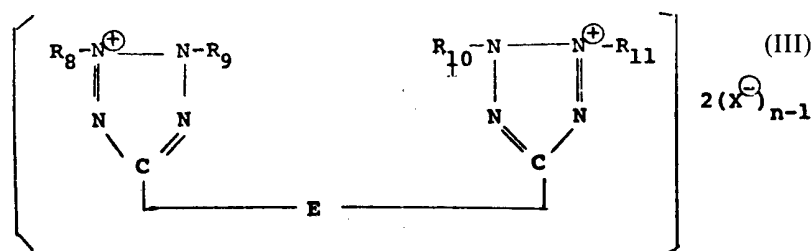
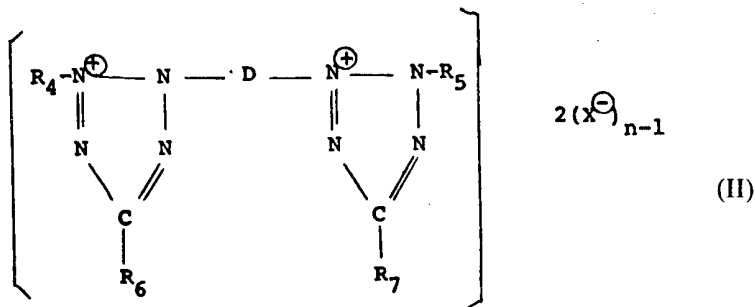
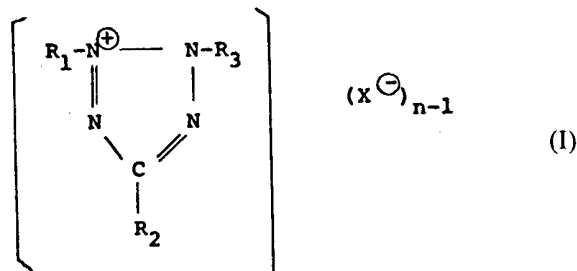
25 Having regard to the provisions of Section 9 of the Patents Act 1949, attention is directed to the claims of our co-pending British Patent Applications No. 31013/76 (Serial No. 1560544) and 31451/77 (Serial No 1,589,594).

25

#### WHAT WE CLAIM IS:—

30 1. A light sensitive silver halide photographic material which comprises a support, at least one hydrophilic colloidal layer coated thereon containing silver halide grains having a number average grain size of from 0.1 to 0.5  $\mu$ , at least 80% of which grains are within a range of from 0.7 to 1.3 times said average grains size, and the silver halide being silver chlorobromide or chloriodobromide containing at least 50 mole % of silver chloride, and a tetrazolium compound of the formula (I), (II), or (III):

30



wherein  $R_1, R_3, R_4, R_5, R_8, R_9, R_{10}$  and  $R_{11}$ , each represents aryl or substituted aryl or a heterocyclic group;  $R_2, R_6$  and  $R_7$ , each represents aryl, substituted aryl, a heterocyclic group, alkyl, substituted alkyl, hydroxyl, carboxyl or a salt thereof, amino, mercapto, cyano, aryl, nitro or hydrogen;  $D$  represents a divalent aromatic group;  $E$  represents alkylene, arylene, or aralkylene;  $X$  is an anion; said heterocyclic group being fur - 2 - yl, thien - 2 - yl, quinol - 2 - yl, benzoxazol - 2 - yl, thiadiazolyl, benzothiadiazolyl, oxazolyl, pyrimidinyl, pyridyl or 2,5 - dimethylthiazolyl; and  $n$  is 1 or 2, provided that the compound forms an intramolecular salt when  $n$  is 1.

2. A light-sensitive silver halide photographic material according to Claim 1 wherein the tetrazolium compound is non diffusible.

3. A light-sensitive silver halide photographic material according to Claim 1 wherein the tetrazolium compound is diffusible.

4. A light-sensitive silver halide photographic material according to any preceding Claim wherein the hydrophilic colloidal layer is a gelatin layer.

5. A light-sensitive silver halide photographic material according to any preceding Claim wherein the tetrazolium compound is present in the hydrophilic colloidal layer.

6. A light-sensitive silver halide photographic material according to any of Claims 1 to 4 wherein the photographic material further comprises a gelatin layer adjacent to the hydrophilic layer, the tetrazolium compound being present in the gelatin layer.

7. A light-sensitive silver halide photographic material according to any preceding Claim wherein the cation moiety of the tetrazolium compound is:

- (1) 2 - (Benzothiazol - 2 - yl) - 3 - phenyl - 5 - dodecyl - 2H - tetrazolium
- (2) 2,3 - Diphenyl - 5 - (4 - t - octyloxyphenyl) - 2H - tetrazolium
- (3) 2,3,5-Triphenyl-2H-tetrazolium
- (4) 2,3,5 - Tri(p - carboxyethylphenyl) - 2H - tetrazolium

- |    |   |    |
|----|---|----|
|    | (5) 2 - (Benzothiazol - 2 - yl) - 3 - phenyl - 5 - (o - chlorophenyl) - 2H - tetrazolium                |    |
|    | (6) 2,3-Diphenyl-2H-tetrazolium   |    |
|    | (7) 2,3-Diphenyl-5-methyl-2H-tetrazolium  |    |
| 5  | (8) 3 - (p - Hydroxyphenyl) - 5 - methyl - 2 - phenyl - 2H - tetrazolium                                | 5  |
|    | (9) 2,3-Diphenyl-5-ethyl-2H-tetrazolium   |    |
|    | (10) 2,3-Diphenyl-5-n-hexyl-2H-tetrazolium  |    |
|    | (11) 5-Cyano-2,3-diphenyl-2H-tetrazolium  |    |
| 10 | (12) 2 - (Benzothiazol - 2 - yl) - 5 - phenyl - 3 - (4 - tolyl) - 2H - tetrazolium                      | 10 |
|    | (13) 2 - (Benzothiazol - 2 - yl) - 5 - (4 - chlorophenyl) - 3 - (4 - nitrophenyl) - 2H - tetrazolium    |    |
|    | (14) 5 - Ethoxycarbonyl - 2,3 - di(3 - nitrophenyl - 2H - tetrazolium                                   |    |
|    | (15) 5-Acetyl-2,3-di(p-ethoxyphenyl)-2H-tetrazolium   |    |
| 15 | (16) 2,5-Diphenyl-3-(p-tolyl)-2H-tetrazolium  | 15 |
|    | (17) 2,5-Diphenyl-3-(p-iodophenyl)-2H-tetrazolium   |    |
|    | (18) 2,3-Diphenyl-5-(p-diphenyl)-2H-tetrazolium   |    |
|    | (19) 5 - (p - Bromophenyl) - 2' - phenyl - 3 - (2,4,6 - trichlorophenyl) - 2H - tetrazolium             |    |
| 20 | (20) 3 - (p - Hydroxyphenyl) - 5 - (p - nitrophenyl) - 2 - phenyl - 2H - tetrazolium                    | 20 |
|    | (21) 5 - (3,4 - Dimethoxyphenyl) - 3 - (2 - ethoxyphenyl) - 2 - (4 - methoxyphenyl) - 2H - tetrazolium  |    |
|    | (22) 5-(4-Cyanophenyl)-2,3-diphenyl-2-H-tetrazolium   |    |
| 25 | (23) 3 - (p - Acetamidophenyl) - 2,5 - diphenyl - 2H - tetrazolium                                      | 25 |
|    | (24) 5-Acetyl-2,3-diphenyl-2H-tetrazolium   |    |
|    | (25) 5-(Fur-2-yl)-2,3-diphenyl-2H-tetrazolium   |    |
|    | (26) 5-(Thien-2-yl)-2,3-diphenyl-2H-tetrazolium   |    |
|    | (27) 2,3-Diphenyl-5-(pyrid-4-yl)-2H-tetrazolium   |    |
| 30 | (28) 2,3-Diphenyl-5-(quinol-2-yl)-2H-tetrazolium  | 30 |
|    | (29) 2,3-Diphenyl-5-(benzoxazol-2-yl)-2H-tetrazolium  |    |
|    | (30) 2,3-Diphenyl-5-nitro-2H-tetrazolium  |    |
|    | (31) 2,2',3,3' - Tetraphenyl - 5,5' - 1,4 - butylene - di - (2H - tetrazolium)                          |    |
|    | (32) 2,2',3,3' - Tetraphenyl - 5,5' - p - phenylene - di - (2H - tetrazolium)                           |    |
| 35 | (33) 2 - (4,5 - Dimethylthiazol - 2 - yl) - 3,5 - diphenyl - 2H - tetrazolium                           | 35 |
|    | (34) 3,5-Diphenyl-2-(triazin-2-yl)-2H-tetrazolium   |    |
|    | (35) 2 - (Benzothiazol - 2 - yl) - 3 - (4 - methoxyphenyl) - 5 - phenyl - 2H - tetrazolium              |    |
| 40 | (36) 2,5-Diphenyl-3- $\alpha$ -naphthyl-2H-tetrazolium, or  | 40 |
|    | (37) 3,3' - (3,3' - Dimethoxy - 4,4' - diphenylene) - 2,2',5,5' - tetraphenyl - di - (2H - tetrazolium) |    |
8. A light-sensitive silver halide photographic material according to any preceding Claim which comprises a protective layer having a thickness of from 0.1 to 10  $\mu$  on the hydrophilic colloidal layer.
9. A light-sensitive silver halide photographic material which comprises a protective gelatin layer having a thickness of from 0.4 to 1.2  $\mu$ .
10. A method of processing a light-sensitive silver halide photographic material according to any preceding Claim, after imagewise exposure to light, which comprises contacting the resulting exposed photographic material with a hydroquinone-containing developing solution.
11. A method according to Claim 10, wherein the developing solution contains Metol.
12. A method according to Claim 10 wherein the developing solution contains 1 - phenyl - 3 - pyrazolidone.
13. A method according to any of Claims 10 to 12 wherein the developing solution contains a sulfite salt in an amount of more than 10 g. per litre.
14. A method according to Claim 13 wherein the pH-value of the developing solution is 8.5 to 12.
15. A light sensitive silver halide photographic material as claimed in Claim 1 substantially as hereinbefore described with reference to any of Examples 1 to 10.
16. A method as claimed in Claim 10 substantially as hereinbefore described with reference to any of Examples 1 to 10.

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