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2-TETRAZOLYLTHIOHYDROQUINONES

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Int. Cl. C07d 55/62, 57/00, 99/10

U.S. Cl. 260—308 D 5 Claims

ABSTRACT OF THE DISCLOSURE

Certain 2-tetrazolylthiohydroquinones and their use as photographic inhibitor releasing developers.

This is a divisional application of U.S. patent application Ser. No. 261,835 of Ralph F. Porter, Judith A. Schwan and John W. Gates, Jr., filed Feb. 28, 1963 and now U.S. Pat. 3,379,529, issued Apr. 23, 1968.

This invention concerns inhibitor-releasing developers and more particularly photographic emulsions containing such developers.

It is well known in the photographic art to employ developing agents in the photographic emulsion. These developing agents can be activated to provide development of the latent image and in some instances to harden or tan the colloid containing the silver halide in the exposed regions which will subsequently form relief images after the unhardened images have been removed. However, the presence of the developing agent in the photographic emulsion may have an adverse effect on the keeping qualities of the emulsion resulting in an overall hardening of the emulsion or fogging. In addition, the developing action carried on by the use of an alkaline agent which initiates development may result in fog or other adverse results. Therefore, it has been desirable to incorporate a development inhibitor agent along with the developer which would reduce fog and improve the keeping characteristics of the photographic emulsion. Preferably, such an inhibitor would also result in inactivating the developer or keeping it in an inactive state until such time that it is needed for carrying out development following exposure.

Hydroquinone has been combined with various materials in the prior art for use as developers or for incorporating in photographic emulsions. For instance, certain compounds of this type have been used wherein it is desired to eliminate and minimize the need for washing or stabilizing operations in liquid photographic baths subsequent to the formation of the silver image, for instance in the diffusion transfer systems, particularly where prints are desired from a silver halide emulsion which has been substantially underexposed in relation to its ASA exposure index. However, these prior art hydroquinone derivatives do not provide inhibitors at the site of development or produce the desired effect of reducing contrast with no loss of speed.

We have found a substituted hydroquinone which, upon activation, produces free hydroquinone and also releases an inhibitor at or near the site of development, resulting in reduced contrast and increased edge effects with little or no loss in speed.

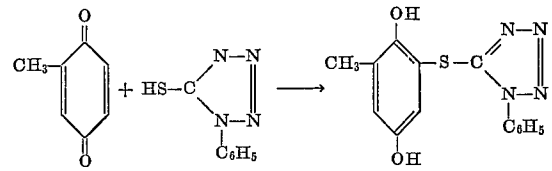
One object of this invention is to provide inhibitor-releasing developers. Another object is to provide photographic emulsions containing inhibitor-releasing developers. A further object is to provide developer containing emulsions having reduced contrast and increased edge

effects with little or no loss in effective speed. A further object is to provide a development inhibitor in chemical combination with a developing agent which releases the inhibitor at or near the site of development. A still further object is to provide aryl or alkyl mercaptotetrazole substituted hydroquinones. Other objects will be apparent from the following disclosure.

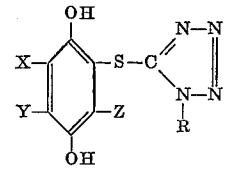
The hydroquinone developers which are useful in our invention are preferably prepared by reacting a p-benzoquinone with a mercaptotetrazole.

The phenylmercaptotetrazole derivatives of hydroquinone are preferably incorporated in the photographic emulsion by forming a dispersion in a high boiling crystalloidal solvent of the type described in Jelley et al., U.S. Pat. 2,322,027. These developers may be substituted in an amount of 5 to 100 mol percent depending upon the particular compound and the desired decrease in contrast.

The following reaction is typical of the general method of preparing these inhibitor-releasing developers (IRD);



The most useful compounds within the scope of our invention have the following general formula:



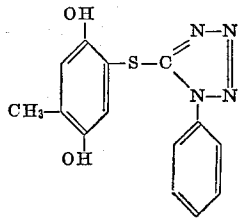
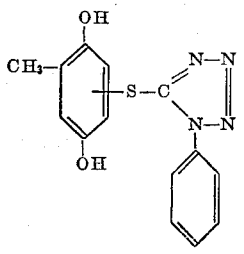
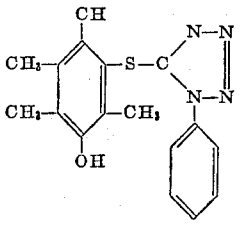
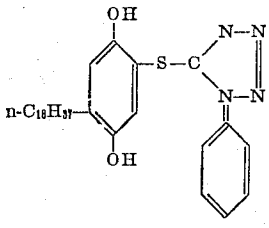
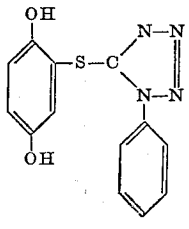
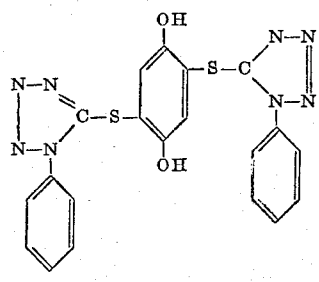
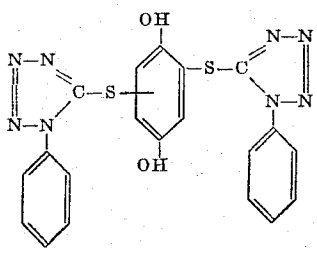
wherein X, Y and Z represent a hydrogen atom, alkyl groups (for example alkyl groups having about 1–20 carbon atoms, such as methyl, butyl, octyl, decyl, tridecyl, eicosyl, etc.), OH, amine, aryl groups (for example aryl groups such as phenyl, tolyl, xylyl, etc.), halogen, heterocyclic groups (for example heterocyclic groups such as tetrazolyl, thiazolyl, quinolinyl, etc.), or mercaptophenyltetrazole and R represents an aryl group (such as phenyl, tolyl, xylyl, etc.) or a lower alkyl group, (for example methyl, ethyl, propyl, butyl, amyl, etc.). X and Y are members of a carbocyclic ring.

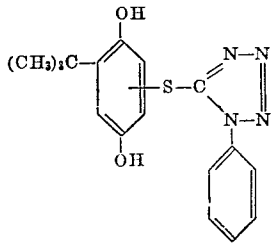
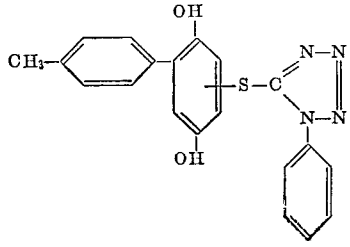
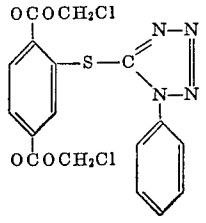
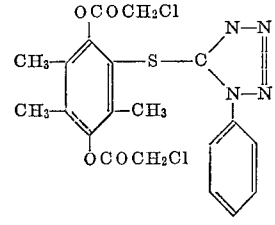
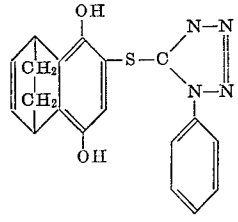
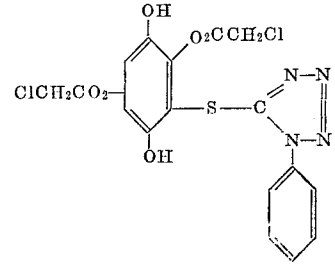
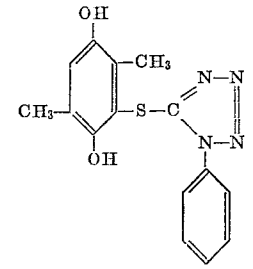
The substituents on the hydroquinone ring are not critical and may be the same or different. Preferably, the substituted hydroquinone will be an active developer. However, the activity of the substituted hydroquinone will depend upon its desired use and may be negligible.

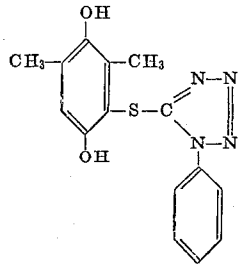
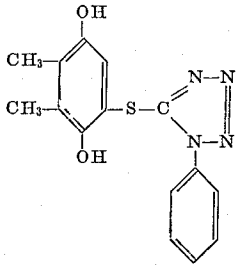
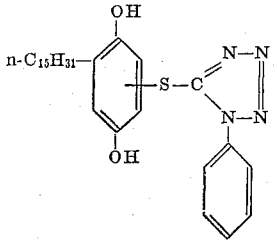
The IRD hydroquinone developers useful in this invention may be prepared as shown by the following preparation of (1 - phenyl - 5 - tetrazolylthio)-p-benzoquinone.

In approximately 20 g. portions p-benzoquinone (86.5 g.) was added to a chilled suspension of 1-phenyl-5-mercaptotetrazole (143 g.) in 500 ml. of methanol. The temperature was maintained below 20° during addition, and after addition was complete the mixture was allowed to stand for 2½ hours. Collection of the solid materials gave 218 g. of white solid (1-phenyl-5-tetrazolylthio) hydroquinone, M.P. 211–212°. The product could be recrystallized from large volumes of acetone to yield white prisms, M.P. 212–216°.

Among the most useful of the inhibiting hydroquinone developers are the following:

Hydroquinone	Structure	Compound Number	Empirical formula	Molecular weight	Melting point, degrees
2-methyl-5-(1-phenyl-5-tetrazolylthio) hydroquinone.		1	$C_{14}H_{12}N_4O_2S$	300.33	178–180
2-methyl-(x)-1-phenyl-5-tetrazolylthio) hydroquinone.		2	$C_{14}H_{12}N_4O_2S$	300.33	199.5–202
1-phenyl-5-tetrazolylthio)trimethyl hydroquinone.		3	$C_{16}H_{16}N_4O_2S$	328.39	184–186.5
2-n-octadecyl-5-(1-phenyl-5-tetrazolylthio)hydroquinone.		4	$C_{31}H_{48}N_4O_2S$	538.78.	155–156.5
(1-phenyl-5-tetrazolylthio)-hydroquinone.		5	$C_{26}H_{10}N_4O_2S$	286.31	212–216
2,5-bis-(1-phenyl-5-tetrazolylthio)-hydroquinone.		6	$C_{20}H_{14}N_8O_2S_2$	462.50	94–95 and 183–187
2,(x)-bis-(1-phenyl-5-tetrazolylthio)hydroquinone.		7	$C_{20}H_{14}N_8O_2S_2$	462.50	213.5–215.5

Hydroquinone	Structure	Compound Number	Empirical formula	Molecular weight	Melting point, degrees
2-t-butyl-(x)-phenyl-5-tetrazolylthio)hydroquinone.		8	$C_{17}H_{18}N_4O_2S$	342.41	166.5–168.5
2-(4-methylphenyl-(x)-(1-phenyl-5-tetrazolylthio)hydroquinone.		9	$C_{20}H_{16}N_4O_2S$	376.3	204–207
1,4-bis-Chloroacetoxy-2-(1-phenyl-5-tetrazolylthio)benzene.		10	$C_{17}H_{12}Cl_2N_4O_4S$	439.28	116.5–118
1,4-bis-chloroacetoxy-2-(1-phenyl-5-tetrazolylthio)-3,5,6-trimethylbenzene.		11	$C_{20}H_{18}Cl_2N_4O_4S$	481.35	95–105
5,8-ethano-2-(1-phenyl-5-tetrazolylthio)-5,8-dihydro-1,4-napthohydroquinone.		12	$C_{19}H_{16}O_2N_4S$	364.28	204–205
2,5-bis-(2-chloroacetoxy)-3-(1-phenyl-5-tertazolylthio)hydroquinone.		13	$C_{17}H_{12}O_6Cl_2N_4S$	471.28	128–131
2,5-dimethyl-3-(1-phenyl-5-tetrazolylthio)hydroquinone.		14	$C_{18}H_{14}O_2N_4S$	314.36	213–4

Hydroquinone	Structure	Compound Number	Empirical formula	Molecular weight	Melting point, degrees
2,6-dimethyl-3-(1-phenyl-5-tetrazolylthio)hydroquinone.		15	$C_{16}H_{14}O_2N_4S$	314.36	188
2,3-dimethyl-5-(1-phenyl-5-tetrazolylthio)hydroquinone.		16	$C_{15}H_{14}O_3N_4S$	314.36	155–7
2-n-pentadecyl-x-(1-phenyl)-5-tetrazolylthio)hydroquinone.		17	{$C_{28}H_{40}O_2N_4S$} {$C_{28}H_{40}O_2N_4S$}	496.63 } 496.63 }	158–685

The following examples are intended to illustrate our invention but not to limit it in any way.

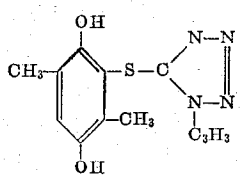
EXAMPLE 1

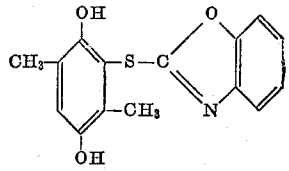
A coating of a silver bromoiodide photographic emulsion having 500 mg. of gel and 300 mg. of silver per sq. ft. is exposed, and developed in a developer containing 0.67 g./l. (67 mol percent) of hydroquinone an 0.87 g./l. (33 mol percent) of (1-phenyl-5-tetrazolylthio)hydroquinone, 0.25 g./l. of Elon, 40 g./l. of sodium sulfite, 25 g./l. of sodium carbonate monohydrate, and 1 g./l. of potassium bromide adjusted to pH 11.5 with sodium hydroxide, for six minutes at 68° and then fixed and washed as usual. Relative to a similar developer but containing 1 g./l. hydroquinone and no thiohydroquinone derivative, this gave a 4 percent reduction in contrast and .07 log E loss in toe speed. X-ray line exposures showed more density at an edge than in an extended exposed area.

EXAMPLE 2

In a test similar to the above and using a variety of compounds, the following results were obtained:

Strips of a silver bromoiodide photographic emulsion coating were exposed on an intensity scale sensitometer and processed according to the precedure given in Example 3, except that only 10 mol percent of the hydroquinone in the check developer was replaced with each of the hydroquinones described as follows:

(A) 

(B) 

Developer A:

	G.
Hydroquinone	1
Elon	.25
Sodium sulfite	40
Sodium carbonate monohydrate	25
Potassium bromide	1

Water to 1 liter.
pH 11.5.

Developer B: As in Developer A, execpt:

	g./l.
Hydroquinone	.90
(A)	.29

Developer C: As in Developer A, except:

	g./l.
Hydroquinone	.90
(B)	.265

The following results were obtained.

Compound	Concentration, mol percent	Speed vs. ck.	Percent of reduction in γ
(A)	10	−.05	15
(B)	10	−.10	3

It can be seen from the above comparison that the phenyl mercapto tetrazole hydroquinone (A) derivative gives considerable reduction in contrast with no significant

loss in speed. The benzoxazolylthiol hydroquinone derivative (B) is much less effective in reducing the contrast of the developed image.

When hydroquinone-phenyl mercapto tetrazole derivatives are compared to other heterocyclic mercaptan-hydroquinones such as hydroquinone derivatives of mercapto benzothiazole, mercapto benzimidazole, mercapto thiazoline, mercapto pyridine and etc., similar advantages are obtained with the hydroquinone-phenyl mercapto tetrazole derivative as described in the comparative example given.

EXAMPLE 3

In a test similar to the above and using a variety of compounds, the following results were obtained:

Compound (HQ)	Concentration, mol percent	Speed vs. ck.	Percent γ reduction
2	10	−.05	−18
1	33	−.14	−27
14	10	−.45	−35
3	5	−.34	−29
5	100	Equal	−27

In all cases a lower minimum density relative to a check developer and increased edge effects were noted.

EXAMPLE 4

By using a developer formula similar to that of Example 1, but replacing the hydroquinone with 0.8 g./l. of 2,5-dimethyl hydroquinone and 0.9 g./l. of 2-methyl-5-(1′-phenyl-5′-tetrazolylthio) hydroquinone, a silver bromoiodide photographic emulsion coating with twice the normal silver halide and gel could be developed to the same speed end contrast as a normal coating through a check developer. An improvement in graininess was obtained.

EXAMPLE 5

A sample of silver bromoiodide film was exposed to X-ray using a knife edge to get a sharp edge. When developed in a formula containing 1 g./l. of hydroquinone, 5.2 g./l. of (1-phenyl-5-tetrazolylthio) hydroquinone, 75 g./l. of sodium sulfite, 30 g./l. of sodium carbonate monohydrate, and 0.1 g./l. of potassium bromide at a pH of 11.5, fog was repressed adjacent to the exposed area. This type of effect in a negative is useful in producing enhanced sharpness in a positive print.

EXAMPLE 6

Coatings

48810 A silver chlorobromide photographic emulsion was coated on a cellulose acetate support at 300 mg. Ag./ft.^{2}. and 692 mg. gel./ft.^{2}.

48814 The same as coating 48810 except just before coating, a dispersion of *x*-methyl-(1-phenyl-5-tetrazolylthio)hydroquinone in N-n-butylacetanilide was added, to yield .025 mole of the hydroquinone per mole of silver halide.

Each of the above coatings was exposed for 1/5″ on an Eastman IB Sensitometer, developed 5′ at 68° F. in Kodak Developer DK–50, rinsed, fixed in Kodak F–5, washed and dried. Another set of film strips was exposed and processed as above except that development was for 4′ in Kodak Developer D–19. Sensitometric results are given below. Speed is measured at a density of 0.30 over fog.

	5′ DK–50			4′ D–19		
Coating	Relative speed	γ	Fog	Relative speed	γ	Fog
48810	111	3.40	.04	102	4.40	.05
48814	104	2.80	.04	97	2.86	.04

Addition of the IRD hydroquinone developer from a coupler solvent dispersion produced contrast reduction with no loss in toe speed.

EXAMPLE 7

Coatings

94–9 Control coating of a silver chlorobromide emulsion on a cellulose acetate support at 300 mg. Ag./ft.^{2} and 692 mg. gel./ft.^{2}.

94–5 The same as coating 94–9 except just before coating a dispersion of trimethyl(1-phenyl-5-tetrazolylthio)-hydroquinone in N-n-butylacetanilide was added, at a concentration of 0.1 mole of the hydroquinone per mole of silver halide.

94–7 The same as coating 94–5 except 0.1 mole of 2-(4-methyl-phenyl)-*x*-(1 - phenyl - 5-tetrazolylthio)hydroquinone was added.

94–8 The same as coating 94–5 except 0.1 mole of 2-n-pentadecyl-*x*-(1 - phenyl-5-tetrazolylthio)hydroquinone was added.

117–1 The same as coating 94–5 except 0.1 mole of 2,5-dimethyl - 3 - (1-phenyl-5-tetrazolylthio)hydroquinone was added.

Each of the above coatings was exposed on an Edgerton Germeshausen and Grier Mark VI Sensitometer and processed as in Example 1.

	5′ DK–50			4′ D–19		
Coating	Relative speed	γ	Fog	Relative speed	γ	Fog
94-9	140	3.08	.05	140	4.20	.05
94-5	146	2.10	.06	146	2.80	.08
94-7	140	1.75	.06	135	3.52	.06
94-8	138	2.76	.05			
117-1	144	2.56	.08			

EXAMPLE 8

Coatings

48952 Same as coating 48810 of Example 6.

48954 Same as coating 48952 but 0.1 mole *x*-methyl-(1-phenyl-5-tetrazolylthio)hydroquinone added from dispersion on N-n-butylacetanilide per mole of silver halide.

48956 Same as coating 48954 but .025 mole added.

48958 Same as coating 48954 but trimethyl-(1-phenyl-5-tetrazolylthio)hydroquinone added.

48959 Same as coating 48958 but 0.25 mole added.

The above coatings were exposed and processed as in Example 6. In addition, X-ray line exposures were made, processed in the same way, and a microdensitometer trace made of the line edge. The coatings containing the thio-substituted hydroquinones had relatively higher line edge densities than the control.

	5′ DK–50			4′ D–19		
Coating	Relative speed	γ	Fog	Relative speed	γ	Fog
48952	111	3.68	.04	107	4.50	.04
48954	90	2.52	.04	96	2.64	.04
48956	103	3.06	.04	102	2.82	.04
48958	111	2.82	.06	112	3.16	.04
48959	112	3.04	.04	116	3.40	.04

The beneficial effects obtained by the IRD hydroquinone developer cannot be obtained by adding the development-inhibitor itself, such as phenylmercaptotetrazole, directly to the emulsion. When the development-inhibitor is added directly to the emulsion, speed losses with no contrast reduction occur even at much lower levels than those used for the IRD thiohydroquinones. With compounds of this type the development-inhibitor appears to be released imagewise, thereby giving the contrast reduction with no speed loss.

EXAMPLE 9

Coatings:

126–5 A silver chlorobromide emulsion was coated on a cellulose acetate support. (Control)

126–1 Similar to the above except just before coating, a dispersion of 2,5-dimethyl-3-(1-phenyl-5-tetrazolylthio)hydroquinone in N-n-butylacetanide was added at a concentration of 0.1 mole of the hydroquinone/mole of the silver halide.

126–3 Similar to the above except just before coating, a dispersion of 3-(2-benzoxazolylthio)-2,5-dimethylhyquinone in N-n-butylacetanilide was added at a concentration of 0.1 mole of the hydroquinone/mole of silver halide.

Each of the above coatings was exposed on an intensity scale sensitometer, developed for five minutes in Kodak Developer D–19, rinsed, fixed in Kodak F–5, washed and dried with the following results:

Coating No.	Relative Speed	γ	Fog
126–5 (control)	123	5.10	.05
126–1	120	3.26	.03
126–3	100	4.80	.07

It can be seen from the above comparison that the preferred PMT-hydroquinone derivative gives an appreciable reduction in contrast with no significant loss of speed whereas other heterocyclic mercaptan-hydroquinone derivatives yield no appreciable reduction in contrast and densensitizes.

EXAMPLE 10

In order to prepare a gelatin overcoat for a color negative, the following dispersion is prepared. A separate dispersion is prepared as a control without any hydroquinone derivative.

PART A

5,8-ethano-2-(1-phenyl-5-tetrazoylthio) - 5,8 - dihydro-1,4-naphthohydroquinone—136 g.
Methyl alcohol—136 ml.
Di-n-butyl phthalate—272 ml.

Heat at 70° C. to dissolve them to cool to 40° C.

PART B

10% gelatin solution—1360 g.
Distilled water—1360 ml.
Mucochloric acid (2.7% aqeous solution)—136 ml.

Heat to 40° C.

Part A is slowly added to Part B with the aid of mechanical agitation. The solution obtained is then passed through a Caton-Gaulin laboratory colloid mill five times. The colloid mill is then rinsed and the dispersion is adjusted to a weight of 3775 g., chill set and stored in a refrigerator.

The above dispersions are then prepared as follows:

A negative element was made in which the top layer of a basic color negative is prepared as follows:

PART I

Dispersion—3775 g.
Distilled water—2225 ml.

Heat to 40° C.

PART II

10% gelatin solution—3180 g.
Distilled water—12,000 ml.
Mucochloric acid (2.7% aqueous solution)—515 ml.

Heat to 40° C., adjust pH to 5.5.

Parts I and II are then combined and diluted with distilled water to 22,700 ml. This solution is coated as the top layer of a basic color negative to yield a coverage of approximately 120 mg. of gelatin per square foot and 40 mg. of the hydroquinone per square foot. This coating is compared to the control coating. After exposure on an intensity scale sensitometer the negatives are processed in an aqueous activator containing 3.5 percent hydroxyethyl cellulose, 4.5 percent NaOH and 2.0 percent benzotriazole, and the released dyes are transferred imagewise to a receiving sheet by lamination in the known manner.

The following illustrates the basic color negative structure as described in U.S. Pat. 2,774,668.

Gelatin overcoat ..... (A)
Blue sensitive bromoiodide emulsion ..... (B)
Yellow dye developer ..... (C)
Gelatin interlayer ..... (D)
Green sensitive bromoiodide emulsion ..... (E)
Magenta dye developer ..... (F)
Gelatin interlayer ..... (G)
Red sensitive bromoiodide emulsion ..... (H)
Cyan dye developer ..... (J)
Support ..... (K)

The receiving sheet is a paper support carrying a gelatino coating containing a mixture of poly-4-vinyl pyridine and 1-phenyl-5-mercaptotetrazole.

The following results show the effectiveness of the thioether hydroquinone as an auxiliary developer compared to the control.

Feature	$D_{min.}$ Red	Blue	Green
Control	.32	.86	.48
Control plus 40 mg. per sq. ft. of 5,8-ethano-2-(1-phenyl-5-tetrazolylthio)-5,8-dihydro-1,4-naphthohydroquinone	.28	.30	.25

The IRD developer compounds of our invention can be incorporated in an ordinary photographic silver halide emulsion, or colloidal dispersion of a water-permeable hydrophilic colloid suitable for preparing an undercoat or an overcoat for such silver halide emulsion, by mixing a solution or dispersion of the developer compound with the halide emulsion, or dispersion of hydrophilic colloid, prior to coating. For example, an IRD developer can be made up as an oil dispersion by stirring a solution of 10 grams of the IRD developing agent into 40 grams of warm tricresylphosphate, and then mixing this solution with 100 grams of a 10 percent aqueous gelatin solution containing 10 ccs. of a 5 percent aqueous solution of an alkynnaphthylene sodium sulfonate wetting agent. The resulting dispersion can then be homogenized by passing for 5 times through a colloid mill to produce a homogeneous colloid dispersion. Solvents other than tricresylphosphate can be employed, including any of the crystalloidal compounds described in Jelley and Vittum U.S. Pat. 2,322,027, issued June 15, 1943. The resulting colloidal dispersion can then be added to a photographic silver halide emulsion, or to a dispersion of a water-permeable hydrophilic colloid, adapted for preparation of an undercoat or overcoat for such silver halide emulsion.

Instead of adding the oil dispersion directly to the liquid silver halide emulsion or colloidal dispersion, it can be dried for storage purposes and then be reconstituted for use by merely mixing with water.

The IRD developing agents of our invention can be adapted for addition to a liquid silver halide emulsion or colloidal dispersion by other means as well. Suitable methods will depend largely upon the solubility characteristics, particularly in water or polar solvents, of the particular precursors in question.

After addition of the dispersion or solution of the IRD developing agent substance to the liquid emulsion or colloidal dispersion, the mixture is stirred to assure uniform results, or passed through a blending device, such as a colloid mill or Waring Blendor. A uniform coating can then be made on a suitable support and the coating dried. Suitable supports comprise any of the well known supporting materials, such as cellulose ester film base (e.g. cellulose acetate, cellulose nitrate, cellulose acetate butyrate, cellulose acetate propionate, etc.), polyethylene, polypropylene, polystyrene, polyethylene terephthalate and other polyesters, paper, polycarbonates, etc.

The photographic elements of our invention comprising a photographic IRD development agent either in the photographic silver halide emulsion layer, or layer contiguous thereto, or both, can then be exposed to an original or negative and developed by merely treating the exposed emulsion layer with an alkaline activator bath. Typical activator baths comprise, for example, an aqueous solution of an alkaline material, such as sodium carbonate, sodium hydroxide, potassium carbonate, potassium hydroxide, mixtures of sodium hydroxide and sodium sulfite, etc. Suitable baths can comprise, for example, an aqueous solution containing about 1 percent sodium hydroxide and 5 percent sodium sulfite. A bath of the latter type is quite suitable for developing an exposed emulsion layer in about 30 seconds when the activator bath is at about 68° F. Modifications can easily be made in the activator baths without departing from the spirit and scope of the invention. For example, an aqueous solution comprising about 4 percent of sodium carbonate and 5 percent of sodium sulfite produces development in about 30 seconds at 68° F. Another aqueous activator solution comprising 2 percent sodium hydroxide and 5 percent sodium sulfite produces useful photographic images in a few seconds when heated at 130° F. Particularly useful activator solutions have a pH of at least about 9.0 and preferably of at least about 10.5.

The activator solutions of the present invention can be applied to an exposed photographic element in any number of known ways, such as by dipping, spraying, or other suitable surface applications. If desired, a thickener can be added to the activator solution to increase the viscosity of the composition and make it more adaptable for continuous processing. Viscous compositions can then be removed by squeegeeing or water spraying. The photographic element can then be stabilized by conventional fixation or stabilization, such as by sodium thiosulfate.

The concentration of the IRD developers used in our invention will vary, depending upon the particular chemical compound involved and the location of the compound within the photographic element. That is, if the IRD developer is incorporated within the silver halide emulsion undergoing development, it may be desirable to use a somewhat different concentration than would be used if the IRD developer were incorporated in a layer contiguous to the photographic silver halide emulsion. A useful concentration of IRD developer for incorporation in the emulsion is from about 0.01 to 4.0 moles per mole of silver halide. A particularly useful range is from about 0.1 to 2.0 moles per mole of silver halide. For incorporation in a layer contiguous to the silver halide emulsion layer, somewhat larger concentrations of IRD developer can be tolerated without adverse effects. A particularly useful effect of our invention is that even when incorporated within the silver halide emulsion, the IRD developers have little or no desensitizing effects. In many cases, this is not true where development-inhibitors or developing agents, per se, are incorporated within the silver halide emulsion layers.

Photographic silver halide emulsions useful in our invention comprise any of the ordinarily employed silver halide developing-out emulsions, such as, silver-chloride, -chlorobromide, -chloroiodide, -chlorobromoiodide, -bromide and -bromoiodide emulsions. Any of the conventionally employed water-permeable hydrophilic colloids can be employed in the silver halide emulsions, or in layer contiguous thereto. Typical water-permeable hydrophilic colloids include gelatin, albumin, polyvinyl alcohol, agar agar, sodium alginate, hydrolyzed cellulose esters, hydrophilic polyvinyl copolymers, etc.

Photographic silver halide emulsions useful in our invention can also contain such addenda as chemical sensitizers, e.g. sulfur sensitizers (e.g. allyl thiocarbamate, thiourea, allyl isothiocyanate, cystine, etc.), various gold compounds (e.g. potassium chloroaurate, auric trichloride, etc.). (See U.S. Pat. 2,540,085, 2,597,856 and 2,597,915), etc.

Photographic silver halide emulsions useful in our invention can also be sensitized by other means, such as by alkylene oxide polymers, many of which are well known to those skilled in the photographic art. Typical polyalkylene oxide polymers include those of U.S. Pat. 2,423,540 and 2,441,389.

The emulsions of the invention can also contain speed-increasing compounds of the quaternary ammonium type as described in U.S. Pats. 2,271,623, issued Feb. 3, 1942; 2,288,226, issued June 30, 1942; 2,334,864, issued Nov. 23, 1943; or the thiopolymers as described in Graham et al. U.S. application Ser. No. 779,839, filed Dec. 12, 1958 and now U.S. Pat. 3,046,129, issued July 24, 1962; and Dann et al., U.S. application Ser. No. 779,874, filed Dec. 12, 1958 and now U.S. Pat. 3,046,134, issued July 24, 1962.

The emulsions may also be chemically sensitized with reducing agents such as stannous salts (Carroll, U.S. Pat. 2,487,850), polyamines such as diethylene triamine (Lowe and Jones, U.S. Pat. 2,518,698), polyamines such as spermine (Lowe and Allen,, U.S. Pat. 2,521,925), or bis-(β-aminoethyl)sulfide and its water-soluble salts (Lowe and Jones, U.S. Pat. 2,521,926).

The emulsions may also be stabilized with the mercury compounds of Allen, Byers and Murray, U.S. application Ser. No. 319,611; Carroll and Murray, U.S. application Ser. No. 319,612; and Leubner and Murray, U.S. application Ser. No. 319,613, all filed Nov. 8, 1952, now U.S. Pats. 2,728,663, 2,728,664 and 2,728,665, respectively, granted Dec. 27, 1955.

The addenda which we have described may be used in various kinds of photographic emulsions. In addition to being useful in x-ray and other nonoptically sensitized emulsions, they may also be used in orthochromatic, panchromatic, and infrared sensitive emulsions. They may be added to the emulsion before or after any sensitizing dyes which are used. The agents may be used in emulsions intended for color photography, for example, emulsions containing color-forming couplers or emulsions to be developed by solutions containing couplers or other color-generating materials, emulsions of the mixed-packet type, such as described in Godowsky, U.S. Pat. 2,698,794, issued Jan. 9, 1955; or emulsions of the mixed-grain type, such as described in Carroll and Hanson, U.S. Pat. 2,592,-243.

It has been found that the development rate of the IRD developers above can be improved by adding an auxiliary developing agent either to the silver halide emulsion layer, or a hydrophilic layer contiguous thereto. Typical auxiliary developing agents include those described in U.S. Pat. 3,312,550, issued Apr. 4, 1967, of P. H. Stewart, G. E. Fallesen and J. W. Reeves, Jr. Typical auxiliary developing agents described in this application include 3-pyrazolidone compounds containing an alkyl (e.g. methyl, ethyl, etc.) or aryl substituent (e.g. phenyl, p-tolyl, etc.). In addition, such pyrazolidone developing agents can contain an acyl or acyloxy substituent which can be hydrolyzed from the 3-pyrazolidone compound by treatment with the above activator solutions to produce the desired auxiliary developing compound. Typical auxiliary developing agents include, for example, 1-phenyl-3-pyrazolidone, 1-p-tolyl-3-pyrazolidone, 1-phenyl-5-methyl-3-pyrazolidone, 1-acetamidophenyl-3-pyrazolidone, 3-acetoxy-1-phenyl-3-pyrazolidone (Enol ester), 2-(pyridinium acetyl)-1-phenyl-3-pyrazolidone chloride, 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-4-methyl-3-pyrazolidone, 1-phenyl-2-benzoyl-3-pyrazolidone, 1-phenyl-2-lauroyl-3-pyrazolidone, 1-phenyl-2-chloroacetyl-3-pyrazolidone, etc.

The concentration of auxiliary developing agents can be varied and, of course, no auxiliary developing agent need be employed unless so desired. Useful concentrations of auxiliary developing agents vary from about 0.01 mole to 2.0 moles based on the IRD developing agent com-

pound. Depending upon the particular auxiliary developing agent employed, larger or smaller quantities can be used.

The IRD developers of our invention can be used in emulsions intended for use in diffusion transfer processes which utilize the undeveloped silver halide in the non-image areas of the negative to form a positive by dissolving the undeveloped silver halide and precipitating it on a receiving layer in close proximity to the original silver halide emulsion layer. Such processes are described in Rott, U.S. Pat. 2,352,014, issued June 20, 1944, and Land, U.S. Pats. 2,584,029, issued Jan. 29, 1952; 2,698,236, issued Dec. 28, 1954, and 2,543,181, issued Feb. 27, 1951; and Yackel et al. U.S. Pat. 3,020,155, issued Feb. 6, 1962. They may also be used in color transfer processes which utilize the diffusion transfer of an imagewise distribution of developer, coupler or dye, from a light-sensitive layer to a second layer, while the two layers are in close proximity to one another. Color processes of this type are described in Land, U.S. Pats. 2,559,643, issued July 10, 1951, and 2,698,798, issued Jan. 4, 1955; Land and Rogers, Belgian Pats. 554,933 and 554,934, granted Aug. 12, 1957; International Polaroid, Belgian Pats. 554,-212, granted July 16, 1957, and 554,935, granted Aug. 12, 1957; Yutzy, U.S. Pat. 2,756,142, granted July 24, 1956, and Whitmore and Mader, U.S. Pat. 3,227,551, issued Jan. 4, 1966. They may also be used in emulsions intended for use in a monobath process such as described in Haist et al., U.S. Pat. 2,875,048, issued Feb. 24, 1959, and in web-type processes, such as the one described in Tregillus et al., U.S. Pat. application Ser. No. 835,473, filed Aug. 24, 1959 and now U.S. Pat. 3,179,517, issued Apr. 20, 1965.

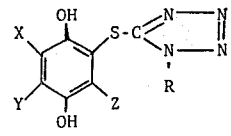
Of course, the activator solutions which are used in our invention are stable for extended periods of time and are not subject to the harmful decomposition reactions so common to conventional photographic developing solutions when these developing solutions are stored for extended periods of time. No special precautions are required to prevent oxidation of the activator solutions since they are inherently quite stable. If desired, the activator solutions can be incorporated in a carrier, such as gelatin and coated in contact with the photographic silver halide emulsion layer which contains the development precursors of our invention. After exposure, the development can be effected merely by heating the photographic emulsion layer to a temperature sufficient to release water, which may be present in the support or in a separate layer in the photographic element. This water then dissolves the activator solution from the hydrophilic colloid layers and takes it into the photographic halide emulsion layer where the emulsion is effected.

The elevated temperatures from about 95–150° C. are usually sufficient to effect development in this manner. If desired, additional moisture can be added by spraying steam upon the sensitive surface of the photographic element.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A compound of the formula:



wherein X and Y represent a member selected from the class consisting of a hydrogen atom, alkyl groups having 1 to 20 carbon atoms, OH, amine, an aryl group containing up to eight carbon atoms, a halogen atom, a heterocyclic group which is one of a tetrazolyl, thiazolyl or quinolinyl group, and when taken together members of a carbocyclic ring, Z represents a member selected from the class consisting of a hydrogen atom, alkyl groups having 1 to 20 carbon atoms, OH, amine, an aryl group containing up to eight carbon atoms, a halogen atom and a heterocyclic group which is one of a tetrazolyl, thiazolyl or quinolinyl group and R represents a member selected from the class consisting of an aryl group having up to eight carbon atoms and a lower alkyl group.

2. 2-methyl-5-(1-phenyl - 5 - tetrazolylthio)hydroquinone.

3. (1-phenyl-5-tetrazolylthio)trimethyl hydroquinone.

4. 2,5 - dimethyl-3-(1-phenyl-5-tetrazolylthio)hydroquinone.

5. 2,6 - dimethyl-3-(1-phenyl-5-tetrazolylthio)hydroquinone.

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260—288 R, 302 H