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**NOVEL PHOTOGRAPHIC PRODUCTS, COMPOSITIONS, AND PROCESSES**

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 No Drawing. Filed Oct. 12, 1960, Ser. No. 62,093  
 29 Claims. (Cl. 96-29)

This application is a continuation-in-part of application Serial No. 663,906, filed June 6, 1957, and now abandoned, and it relates to photography and, more particularly, to compositions and processes useful in the development of photosensitive silver halide elements.

It is one object of the present invention to provide novel products, developer compositions and processes employing such novel products and developer compositions for the development of silver halide emulsions.

A further object of this invention is to provide novel products and developer compositions useful in diffusion-transfer-reversal processes, and particularly in high-speed, diffusion-transfer-reversal processes wherein the silver halide emulsion has been underexposed in relation to its ASA rating.

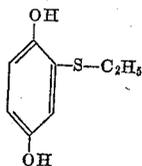
The invention accordingly comprises the several steps and the relation and order of one or more of such steps with respect to each of the others, and the products and compositions possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

We have discovered a novel class of silver halide developing agents represented by the formula:

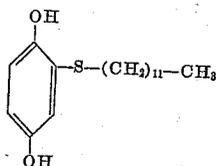


wherein R may be an alkyl group, preferably a 1-12 carbon alkyl group such as methyl, ethyl, isopropyl, etc., an aryl group, a substituted alkyl group, e.g., substituted with an acid such as carboxy, or with an aryl group, a substituted aryl group, preferably substituted with a halogen such as chlorine or a lower alkyl group such as methyl, ethyl, isopropyl, etc. or a heterocyclic group; each Z is a halogen such as chlorine, an alkyl, preferably a lower alkyl such as methyl, ethyl, isopropyl, etc. or an aryl group; n is 0, 1, 2 or 3; and Ar is a 2,5-dihydroxyphenyl group.

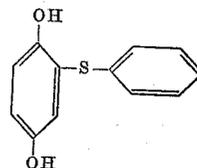
The following compounds are examples of developing agents within the scope of this invention:



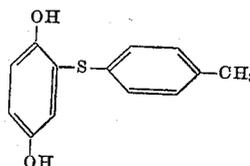
(1) 2-(ethyl-thio)-hydroquinone (2-ethyl-thio-1,4-dihydroxy benzene)



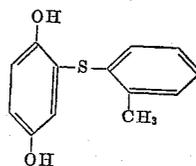
(2) 2-(dodecyl-thio)-hydroquinone (2-dodecyl-thio-1,4-dihydroxy benzene)



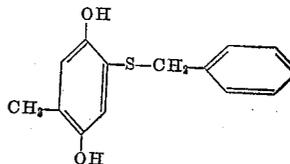
(3) 2-(phenyl-thio)-hydroquinone (2-phenyl-thio-1,4-dihydroxy benzene)



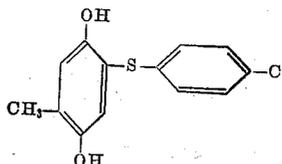
(4) 2-(p-tolyl-thio)-hydroquinone (2-p-tolyl-thio-1,4-dihydroxy benzene)



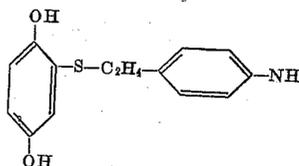
(5) 2-(o-tolyl-thio)-hydroquinone (2-o-tolyl-thio-1,4-dihydroxy benzene)



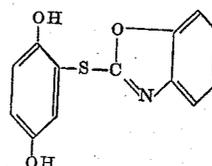
(6) 2-(benzyl-thio)-toluhydroquinone (2-benzyl-thio-5-methyl-1,4-dihydroxy benzene)



(7) 2-(p-chlorophenyl-thio)-toluhydroquinone (2-p-chlorophenyl-thio-5-methyl-1,4-dihydroxy benzene)

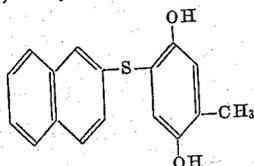


(8) 2-(p-amino-phenethyl-thio)-hydroquinone (2-p-amino-phenethyl-thio-1,4-dihydroxy benzene)

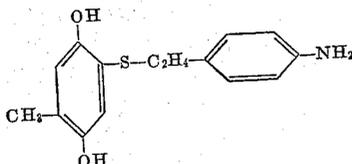


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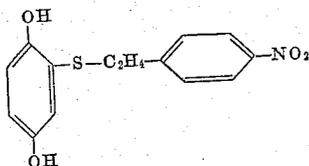
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(9) 2-(2'-benzoxazole-thio)-hydroquinone (2-(2'-benzoxazolyl-thio)-1,4-dihydroxy benzene)



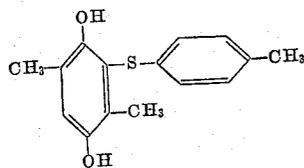
(10) 2-(β-naphthyl-thio)-toluhydroquinone (2-β-naphthyl-thio-5-methyl-1,4-dihydroxy benzene)



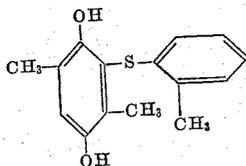
(11) 2-(p- amino-phenethyl - thio) - toluhydroquinone (2-p-aminophenethyl-thio - 5 - methyl-1,4-dihydroxy benzene)



(12) 2-(p-nitro-phenethyl-thio)-hydroquinone (2-p-nitrophenethyl-thio-1,4-dihydroxy benzene)



(13) 2-(p-tolyl-thio)-3,6-dimethyl-hydroquinone (2-p-tolyl-thio-3,6-dimethyl-1,4-dihydroxy benzene)



(14) 2-(o-tolyl-thio)-3,6-dimethyl-hydroquinone (2-o-tolyl-thio-3,6-dimethyl-1,4-dihydroxy benzene)

The illustrated alkyl-thio-hydroquinone developing agents of this invention may be prepared according to the procedures of Alcaley in *Helv. Chem. Acta* 30, pages 578 to 584 (1949). p-Aminophenethyl-thio-hydroquinone (compound 8), p-aminophenethyl-thio-toluhydroquinone (compound 11) and p-nitrophenethyl-thio-hydroquinone (compound 12) are novel compounds and are prepared according to the procedure disclosed and claimed in our copending application Serial No. 663,876, filed June 6, 1957, now U.S. Patent No. 3,009,958, issued November 21, 1961. The illustrated aryl and heterocyclic thio-hydroquinone developing agents may be prepared by the addition of one mole of quinone to one mole of compounds of the general formula R-SH wherein R is the desired aryl or heterocyclic configuration.

As a further illustration of heterocyclic thio-hydroquinones which may be used as developing agents in the practice of this invention, mention may be made of the compounds disclosed in U.S. Patent No. 2,616,893, issued on November 4, 1952.

In addition thereto, and as illustrative of compounds of the general formula R-SH which may be utilized, in accordance with the above-mentioned addition reaction, to

form heterocyclic thio-hydroquinone developing agents, mention may be made of the following mercaptans: 2-mercapto benzthiazole; 2-mercapto benzimidazole; 1-methyl-2-mercapto imidazole; 2-mercapto thiazoline; 5-methyl-2-mercapto oxazoline; 2-mercapto pyridine; and 2-mercapto barbituric acid.

It is to be noted that the heterocyclic compounds described above for purposes of illustration contain at least one carbon atom in the heterocyclic nucleus. In other words, they may be defined as thio-hydroquinone developing agents having a carbon-containing heterocyclic radical attached to the sulfur atom.

As was mentioned previously, the silver halide developing agents of this invention may be represented by the 15 formula:



wherein each of Z, n, Ar and R have the meanings heretofore given. It should be apparent, therefore, that the invention is not limited to the illustrative compounds previously described. As will be apparent to those skilled in the art, the alkyl and aryl groups may be substituted, if desired, since the aryl and/or alkyl group will act as an insulator against any hindering substituent which may be present. As will also be apparent to those skilled in the art, heterocyclic groups other than those specifically disclosed may likewise be employed, since a heterocyclic group will function in a manner similar to an aryl group and, accordingly, will not hinder the developing function of the hydroquinonyl nucleus.

The novel silver halide developing agents of this invention are useful in conventional black-and-white development and in diffusion transfer-reversal processes, both dye and silver, and are especially useful in such photographic processes wherein it is desired to eliminate or minimize the need for washing or stabilizing operations in liquid baths subsequent to the formation of the silver print. Examples of such diffusion-transfer processes are disclosed in U.S. Patents Nos. 2,543,181 and 2,647,056 issued to Edwin H. Land.

In particular, certain of the novel developing agents of this invention are highly useful in so-called "high-speed" diffusion-transfer-reversal processes wherein high quality silver transfer prints are obtained from a silver halide emulsion which has been substantially underexposed in relation to its ASA exposure index. Such an exposure provides a latent image having a density gradient confined to the low exposure or toe region of the negative material's characteristic curve. Processes of this type are disclosed and claimed in the copending application of Edwin H. Land et al, Serial No. 564,492, filed February 9, 1956.

The expression "equivalent overall speed," as set forth herein, indicates generally the correct exposure rating or exposure index to which an ASA exposure meter must be set in order that it give correct exposure data for producing positive pictures of satisfactory high quality by the silver-transfer-reversal process.

The invention will be illustrated in greater detail in conjunction with the following specific examples which set out representative use of the novel developers of this invention in "high-speed," diffusion-transfer-reversal processes, but is not limited to the details set forth, which are intended to be illustrative only.

#### Example I

A silver iodobromide emulsion sold by Eastman Kodak under the trade name "Royal Pan" was exposed to a subject through a stop which gives rise to an equivalent overall speed of 1500 reciprocal meter-candle-seconds [m.c.s.], advanced in superposed relationship with an image-receiving element, comprising a silver-receptive stratum containing silver precipitating nuclei dispersed in a matrix of colloidal silica coated on a water-impervious base according to the practice described in U.S. Patent No. 2,823,122, issued to Edwin H. Land, between a pair of pres-

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sure-applying rollers to spread the processing composition comprising:

	G.
Sodium carboxymethyl cellulose-----	13.35
Sodium hydroxide-----	10.64
Chlorobenzotriazole-----	5.9
Sodium sulfite-----	17.10
Sodium thiosulfate-----	3.60
p-Tolyl-thio-hydroquinone-----	9.0
Water-----	265.50

between them in a thin layer approximately 0.003 of an inch thick. After an imbibition period of approximately sixty seconds, the emulsion, together with the layer of processing composition, was stripped from the image-receiving element to uncover the positive print, which had satisfactory contrast, density and range.

The equivalent overall speed obtained by using 11.4 g. of hydroquinone in the process of Example I was 100 reciprocal m.c.s.

#### Example II

A silver iodobromide emulsion sold by Eastman Kodak under the trade name "Royal Pan" was exposed to a subject through a stop which gave rise to an equivalent overall speed of 1000 reciprocal m.c.s. and processed according to the procedure of Example I in which o-tolyl-thio-hydroquinone was substituted for p-tolyl-thio-hydroquinone.

Similarly, high equivalent overall speeds may be obtained by the use of a photographic developer composition containing either 2-p-tolyl-thio-3,5-dimethyl-hydroquinone or 2-o-tolyl-thio-3,5-dimethyl-hydroquinone.

The novel silver halide developing agents of this invention are also useful in diffusion-transfer processes of the type wherein the silver precipitating nuclei are contained in the processing fluid so that the solidified layer of said fluid contains the desired silver transfer image, in accordance with the principles of U.S. Patent No. 2,662,822, issued to Edwin H. Land on December 15, 1953.

It will be apparent that the relative proportions of the novel agents of the developer composition set forth above may be altered to suit the requirements of the operator; thus, it is within the scope of this invention to modify the above developing composition by the substitution of preservatives, alkalis, silver halide solvents, etc., other than those specifically mentioned. When desirable, it is also contemplated to include in the developing composition common components such as restrainers, accelerators, etc., as well as additional silver halide developing agents. Similarly, the concentration of the developing agent may be varied over a wide range and when desirable the developing agent may be disposed in the photosensitive emulsion prior to the exposure of said emulsion.

This invention thus provides a new class of silver halide developing agents. Their usefulness is particularly unexpected in view of the generally accepted belief that use of sulfur-containing reagents has a deleterious effect in photographic processes. It is particularly unexpected that these developing agents would provide high equivalent overall speeds, such as are obtained with these compounds, and particularly with the alkaryl thio-substituted hydroquinones and alkyl-hydroquinones which constitute a preferred group.

Since certain changes may be made in the above products, compositions and processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic developer composition comprising an aqueous solvent, an alkaline material soluble therein, a silver halide solvent-fixer, and a silver halide developing

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agent selected from the group consisting of compounds within the formula:



5 where Ar is a 2,5-dihydroxyphenyl radical and R is a member of the group consisting of a carbon-containing heterocyclic, an alkyl, a phenyl and a naphthyl radical.

2. A photographic developer composition as defined in claim 1, wherein said silver halide developing agent is 2-p-tolyl-thio-1,4-dihydroxy benzene.

3. A photographic developer composition as defined in claim 1, wherein said silver halide developing agent is 2-o-tolyl-thio-1,4-dihydroxy benzene.

4. A photographic developer composition as defined in claim 1, wherein said silver halide developing agent is 2-p-tolyl-thio-3,6-dimethyl-1,4-dihydroxy benzene.

5. A photographic developer composition as defined in claim 1, wherein said silver halide developing agent is 2-o-tolyl-thio-3,6-dimethyl-1,4-dihydroxy benzene.

6. A photographic developer composition as defined in claim 1, wherein said silver halide developing agent is 2-ethyl-thio-1,4-dihydroxy benzene.

7. A photographic process which comprises the steps of developing an exposed silver halide emulsion with an aqueous alkaline solution of a silver halide developing agent of the formula:



30 wherein Ar is a 2,5-dihydroxyphenyl radical and R is a member of the group consisting of a carbon-containing heterocyclic, an alkyl, a phenyl and a naphthyl radical; providing an imagewise distribution of mobile image-forming components in the undeveloped areas thereof as a function of and under the control of development; and transferring at least part of said imagewise distribution, by imbibition, to a contiguous image-receiving material to impart a transfer image to said image-receiving material.

8. A photographic process which comprises the steps of developing an exposed silver halide emulsion with an aqueous solution comprising an alkaline material and a silver halide developing agent of the formula:



45 wherein Ar is a 2,5-dihydroxyphenyl radical and R is a member of the group consisting of a carbon-containing heterocyclic, an alkyl, a phenyl and a naphthyl radical; reacting unreduced and undeveloped silver halide therein with a silver halide solvent-fixer, thus providing an imagewise distribution of a soluble silver complex; and transferring at least part of said imagewise distribution, by imbibition, to a contiguous image-receiving material to impart a positive silver image to said image-receiving material.

9. A process as defined in claim 7, wherein said silver halide developing agent is 2-p-tolyl-thio-1,4-dihydroxy benzene.

10. A process as defined in claim 7, wherein said silver halide developing agent is 2-o-tolyl-thio-1,4-dihydroxy benzene.

11. A process as defined in claim 7, wherein said silver halide developing agent is 2-p-tolyl-thio-3,6-dimethyl-1,4-dihydroxy benzene.

12. A process as defined in claim 7, wherein said silver halide developing agent is 2-o-tolyl-thio-3,6-dimethyl-1,4-dihydroxy benzene.

13. A process as defined in claim 7, wherein said silver halide developing agent is 2-ethyl-thio-1,4-dihydroxy benzene.

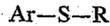
14. A process as defined in claim 7, wherein said developing agent is disposed prior to exposure in a photosensitive element containing said emulsion and the solution containing said developing agent is formed by permeating said photosensitive element with an aqueous alkaline liquid capable of solubilizing said developing agent.

15. A process as defined in claim 7, wherein said de-

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veloping agent is dissolved prior to exposure in an aqueous alkaline solution.

16. A method of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion with an aqueous solution comprising an alkaline material and a silver halide developing agent of the formula:



wherein Ar is a 2,5-dihydroxyphenyl radical and R is a member of the group consisting of a carbon-containing heterocyclic, an alkyl, a phenyl and a naphthyl radical.

17. A method as defined in claim 16, wherein said silver halide developing agent is 2-p-tolyl-thio-1,4-dihydroxy benzene.

18. A method as defined in claim 16, wherein said silver halide developing agent is 2-o-tolyl-thio-1,4-dihydroxy benzene.

19. A method as defined in claim 16, wherein said silver halide developing agent is 2-p-tolyl-thio-3,6-dimethyl-1,4-dihydroxy benzene.

20. A method as defined in claim 16, wherein said silver halide developing agent is 2-o-tolyl-thio-3,6-dimethyl-1,4-dihydroxy benzene.

21. A method as defined in claim 16, wherein said silver halide developing agent is 2-ethyl-thio-1,4-dihydroxy benzene.

22. A method as defined in claim 16, wherein said developing agent is disposed prior to exposure in a photosensitive element containing said emulsion and the solution containing said developing agent is formed by permeating said photosensitive element with an aqueous alkaline liquid capable of solubilizing said developing agent.

23. A method as defined in claim 16, wherein said developing agent is dissolved prior to exposure in an aqueous alkaline solution.

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24. A photographic product comprising a support, a silver halide emulsion in a layer carried by said support, and a silver halide developing agent in a layer on the same side of said support as said silver halide emulsion, said developing agent being a compound of the formula:



wherein Ar is a 2,5-dihydroxyphenyl radical and R is a member of the group consisting of a carbon-containing heterocyclic, an alkyl, a phenyl and a naphthyl radical.

25. A photographic product as defined in claim 24, wherein said silver halide developing agent is 2-p-tolyl-thio-1,4-dihydroxy benzene.

26. A photographic product as defined in claim 24, wherein said silver halide developing agent is 2-o-tolyl-thio-1,4-dihydroxy benzene.

27. A photographic product as defined in claim 24, wherein said silver halide developing agent is 2-p-tolyl-thio-3,6-dimethyl-1,4-dihydroxy benzene.

28. A photographic product as defined in claim 24, wherein said silver halide developing agent is 2-o-tolyl-thio-3,6-dimethyl-1,4-dihydroxy benzene.

29. A photographic product as defined in claim 24, wherein said silver halide developing agent is 2-ethyl-thio-1,4-dihydroxy benzene.

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

2,543,181	Land	Feb. 27, 1951
2,647,056	Land	July 28, 1953

##### OTHER REFERENCES

James et al., J.A.C.S., 61, 442-450 (1939).
Schubert, J.A.C.S. 69, 712-713 (1947).
Webster's New International Dictionary Unabridged, 2d Edition.

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,043,690

July 10, 1962

Milton Green et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 72, for "dihydrogen" read -- dihydroxy --;  
column 6, line 5, for "where" read -- wherein --.

Signed and sealed this 30th day of April 1963.

(SEAL)

Attest:

ERNEST W. SWIDER  
Attesting Officer

DAVID L. LADD  
Commissioner of Patents