United States Patent

Buckler et al.

[15] **3,640,713**

[45] **Feb. 8, 1972**

[54] PHOTOGRAPHIC PROCESSES AND COMPOSITIONS THEREFOR

[72] Inventors: **Sheldon A. Buckler,** Lincoln; **Ronald F. Lambert,** Cambridge, both of Mass.

[73] Assignee: **Polaroid Corporation,** Cambridge, Mass.

[22] Filed: **Oct. 30, 1968**

[21] Appl. No.: **772,017**

[52] **U.S. Cl.** **96/29,** 96/61, 96/66

[51] **Int. Cl.** **G03c 5/54**

[58] **Field of Search** 96/66.3, 29, 109, 66, 61

[56] **References Cited**

UNITED STATES PATENTS

2,543,181	2/1951	Land	96/29
2,647,056	7/1953	Land	96/29
3,019,108	1/1962	Dershowitz	96/66.3
3,236,644	2/1966	Gilman et al.	96/29
3,311,473	3/1967	Foster et al.	96/29

Primary Examiner—Murray Katz
Assistant Examiner—Bernard D. Pianalto
Attorney—Brown and Mikulka and Sybil A. Campbell

[57] **ABSTRACT**

Tertiary organic phosphines containing a hydroxyl and/or an amino-substituted phenyl group are used as silver halide developing agents in photographic processing compositions which find particular utility in diffusion transfer photographic techniques.

11 Claims, No Drawings

PHOTOGRAPHIC PROCESSES AND COMPOSITIONS THEREFOR

This invention 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 developer compositions and processes employing the same for the development of exposed silver halide emulsions.

A further object of this invention is to provide novel developer compositions which are particularly useful in diffusion transfer processes.

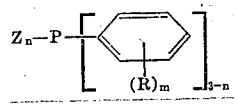
Other objects of the invention will in part be obvious and will in part appear hereinafter.

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 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.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

In copending application of Stanley M. Bloom Ser. No. 699,300, filed Jan. 22, 1968 and now U.S. Pat. No. 3,578,449, organic derivatives of the trihydrides of trivalent elements in Group VA of the Periodic Table are disclosed and claimed as silver halide solvents for use in photographic processing compositions. Included in this class of silver halide solvents are organic phosphines.

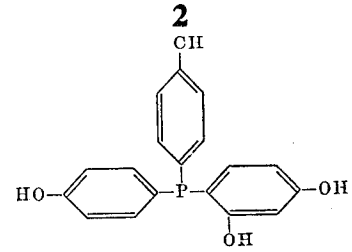
It has now been discovered that certain of these phosphines, namely, tertiary organic phosphines containing a hydroxyl and/or an amino-substituted phenyl group also may be used as agents for developing exposed silver halide emulsions. These developing agents may be represented by the formula:

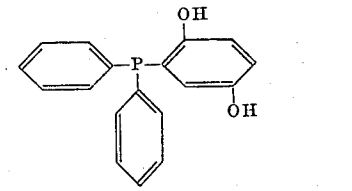


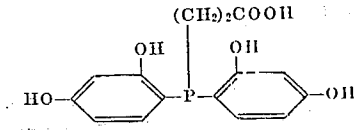
wherein Z is a monovalent hydrocarbon radical or a monovalent substituted hydrocarbon radical, i.e., a hydrocarbon radical substituted with atoms or groups containing atoms other than carbon and hydrogen; R, the same or different, is a hydroxyl group or an amino group which may be a primary, secondary or tertiary amino group, i.e., NR''_2 wherein R'', the same or different, is selected from hydrogen, lower alkyl, i.e., having one to six carbon atoms, or phenyl; *m* is at least 1; and *n* is an integer 0, 1 or 2. In the above formula, the hydrocarbon or substituted hydrocarbon radical, Z, may be aryl such as phenyl or naphthyl which in turn may be substituted with alkyl, alkoxy, halogen, cyano, nitro, amino, carboxyl, hydroxyl, sulfonyl and so forth; or alkyl having one to **20** carbon atoms such as methyl, ethyl, butyl, octyl, decyl, dodecyl, etc., which also may contain the substituents enumerated above, and especially an alkyl such as $-(CH_2)_pX$ wherein *p* is an integer of 2 to 4, inclusive, X is selected from —COOR', —COR', —NO_2, —CN, $-SO_3R'$ and R' is selected from hydrogen, alkyl, preferably lower alkyl, substituted or unsubstituted; and aryl, preferably phenyl, substituted or unsubstituted. For use in aqueous photographic systems as conventionally employed, the hydrocarbon and substituted hydrocarbon radicals selected typically are such as to render the compound soluble in aqueous alkali.

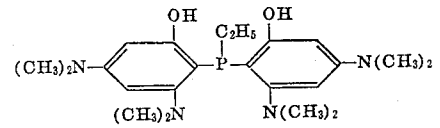
In a preferred embodiment of the present invention, the compounds encompassed by the above formula contain at least one phenyl group substituted with at least two R groups which are in the ortho or para positions to each other. Thus, the arrangement of R groups may be 2,5; 3,4; 2,3,5; and so forth as exemplified by 2,5-dihydroxy; 2,5-diamino; 2,5-dimethylamino; 3,4-dihydroxy; 2,3,5-trihydroxy; 2,3-dihydroxy-5-methylamino and the like.

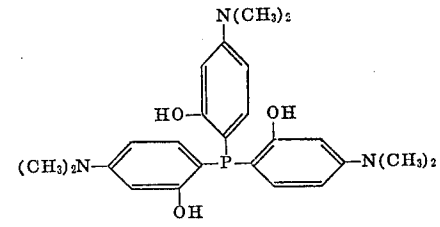
Examples of particular compounds useful in the present invention are as follows:

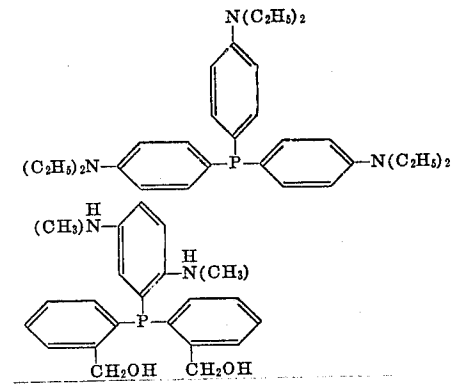


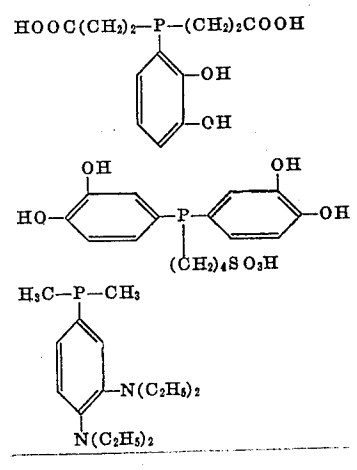












Though triphenyl phosphonium halides have been disclosed and claimed as photographic developing agents in U.S. Pat. No. 3,019,108, like most of the developing agents in common use, they are satisfactory under alkaline processing conditions but tend to be ineffective in neutral media. In comparison, the phosphine developing agents of the present invention are effective not only under alkaline conditions but in neutral solution as well. The greater latitude afforded by the compounds of the present invention is a distinct advantage since neutral photographic processing compositions are considerably more stable upon exposure to the atmosphere and thus, do not require the same degree of care in handling and storage prior to and during use.

As indicated above, the novel developing agents of the present invention while useful in conventional or "tray" development find particular utility in diffusion transfer processes. Such processes are now well known in the art; see, for example, U.S. Pat. Nos. 2,543,181; 2,647,056; etc. In processes of this type, an exposed silver halide emulsion is treated with a processing composition whereby the exposed silver halide is developed and an imagewise distribution of diffusible image-forming components is formed as a function of the point-to-point development. This distribution of image-forming components is transferred by inhibition to an image-receiving stratum in superposed relationship with the emulsion to form a transfer image thereon. In diffusion transfer processes where a silver image is formed, processing is effected in the presence of a silver halide solvent, such as sodium thiosulfate, which forms a diffusible complex with the undeveloped silver halide. In preparing silver prints in this manner, the image-receiving element preferably includes a silver precipitating agent, as is well known in the art.

The following examples are given to further illustrate the present invention and are not intended to limit the scope thereof.

EXAMPLE 1

A gelatino silver iodobromide emulsion was exposed and processed with a composition prepared by adding 0.6 g. of 2,5-dihydroxyphenyl-bis(diphenyl)phosphine to 10 cc. of a composition comprising:

Hydroxyethyl cellulose	366 g.
Sodium hydroxide	425 g.
6-nitrobenzimidazole nitrate	10.8 g.
Potassium iodide	15 g.
sodium sulfite	260 g.
Sodium thiosulfate	741 g.
Gum arabic	100 cc.
Water	8,289 g.

The image-receiving element comprised a silver-receptive stratum containing silver-precipitating nuclei dispersed in a matrix of colloidal silica coated on a water-impervious base. The exposed emulsion and the image-receiving element were advanced in superposed relationship between a pair of pressure-applying rollers to spread the processing solution between them in a layer about 0.0022 inch thick. After an inhibition period of approximately 60 seconds, the emulsion element was stripped from the image-receiving element to reveal a good quality positive print.

EXAMPLE 2

A gelatino silver iodobromide emulsion was exposed to a step tablet and processed by spreading a layer of processing composition approximately 0.0030 inch thick between the thus exposed emulsion and an image-receiving element of the type used in Example 1 above. The processing composition employed was prepared by addition 0.6 g. of 2,5-dihydroxyphenyl-bis(diphenyl)phosphine to the following formulation:

Hydroxyethyl cellulose	5.0 g.
Triethanolamine	0.56 g.
Zinc acetate	1.5 g.
Potassium hydroxide	1.5 g.
Uracil	0.8 g.
Water	10.0 g.

After an inhibition period of about 30 seconds, the emulsion and image-receiving elements were separated and the silver receptive layer was found to have a good quality positive silver transfer image exhibiting good contrast.

In a further experiment, the organic phosphine used in the above examples was admixed with silver nitrate in alcohol solution. Within a few seconds a fine silver deposit was formed. Similar results were obtained when the same organic phosphine was admixed with silver ethylenediaminetetraacetate in aqueous solution at pH 5.6.

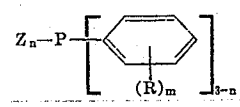
It will be apparent that the relative proportions of the novel developing agents of the above processing compositions may be varied to suit the requirements of the operator and that they will be used in amounts effective to achieve the desired results in a given system. Also, it is within the scope of this invention to modify the formulations set forth above by the substitution of alkalies, silver halide solvents, antifoggants, etc., other than those specifically mentioned. Where desirable, it is also contemplated to include in the compositions, accelerators or other components as commonly used in the art.

While the phosphine developing agent has been employed in the processing solutions in the examples set out above, it will be understood that the developing agent may be initially located in a layer of the photosensitive element, for example, in the silver halide emulsion stratum itself or in another layer adjacent thereto. For example, by selecting appropriate Z substituents such as a long chain alkyl group substantially nondiffusing developing agents may be obtained. In this instance the processing composition containing the developing agent is formed by permeating the photosensitive element with nonaqueous media capable of solubilizing the agent.

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

What is claimed is:

1. A photographic developer composition comprising an aqueous solution containing a silver halide solvent and a silver halide developing agent selected from the group consisting of compounds within the formula

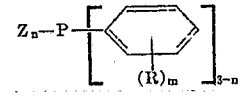


wherein Z is a monovalent hydrocarbon radical, substituted or unsubstituted; R is selected from a hydroxyl group and an amino group; *m* is at least 1; and *n* is an integer 0, 1 or 2.

2. A composition as defined in claim 1 wherein *m* is 2 and said R groups are in para position to each other.

3. A composition as defined in claim 1 wherein said developing agent is 2,5-dihydroxyphenyl-bis(diphenyl)-phosphine.

4. A method of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion containing a latent image with an aqueous solution containing a silver halide developing agent selected from the group consisting of compounds within the formula

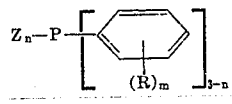


wherein Z is a monovalent hydrocarbon radical, substituted or unsubstituted; R is selected from a hydroxyl group and an amino group; *m* is at least 1; and *n* is an integer 0, 1 or 2.

5. A method according to claim 4 wherein *m* is 2 and said R groups are in para position to each other.

6. A method according to claim 4 wherein said developing agent is 2,5-dihydroxyphenyl-bis(diphenyl)phosphine.

7. A photographic process comprising the steps of developing an exposed silver halide emulsion with an aqueous solution comprising a silver halide developing agent and a silver halide solvent in the presence of an image-receiving material superposed on said silver halide emulsion to form a silver transfer print on said image-receiving material, said developing agent being selected from the group consisting of compounds represented by the formula



wherein Z is a monovalent hydrocarbon radical, substituted or unsubstituted; R is selected from a hydroxyl group and an amino group; *m* is at least 1; and *n* is an integer 0, 1 or 2.

8. A process according to claim 7 wherein said developing agent is 2,5-dihydroxyphenyl-bis(diphenyl)phosphine.

9. A composition as defined in claim 2 wherein both of said R groups are hydroxyl groups.

10. A method according to claim 5 wherein both of said R groups are hydroxyl groups.

11. A process according to claim 7 wherein *m* is 2 and said R groups are hydroxyl groups in para position to each other.

* * * * *