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3,019,108

PHOTOGRAPHIC PROCESS, PRODUCTS AND COMPOSITIONS

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6 Claims. (Cl. 96—66)

This invention relates to photography and more particularly to photographic developing compositions and processes.

It is one object of the present invention to provide processes and photographic developing agents and compositions for the development of photosensitive silver halide emulsions.

Another object of the present invention is to provide photographic developing agents and compositions particularly useful in diffusion transfer processes.

Still another object of the present invention is to provide low mobility photographic developing agents especially useful in one-step photographic processes for forming color images.

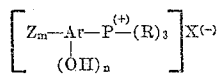
Still another object of the present invention is to provide photographic products, particularly photosensitive elements employing photographic developing agents of the above type.

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

The invention accordingly comprises the process involving 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.

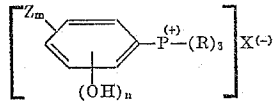
For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

Specifically, the photographic developing agents comprehended by the present invention may be represented by the general formula comprising:



wherein Ar is an aryl nucleus such as a benzene or naphthalene nucleus, n is at least two, Z is an alkyl group such as methyl, ethyl, octyl, and the like, or a halogen group such as chlorine or an alkoxy group such as methoxy and ethoxy, m is an integer including zero, R is a phenyl group and X is a halogen group such as chlorine.

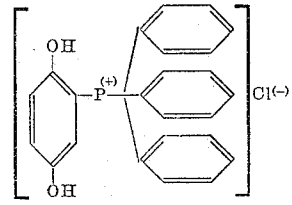
In one preferred embodiment the aryl nucleus Ar is a benzene nucleus and such compounds may be represented by the formula comprising:



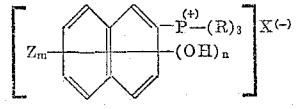
wherein Z, m, R, X and n have the same meaning as above.

It will be noted that all the compounds contain at least two hydroxy groups. These hydroxy groups are in the ortho or para positions to each other. Thus, the hydroxy arrangement present may be a 2,5-dihydroxy, a 3,4-dihydroxy, a 2,3,5-trihydroxy and the like. The polyhydroxyphenyl group may also contain alkyl, alkoxy, and halogen groups. One preferred compound of

this class is 2,5-dihydroxyphenyltriphenyl phosphonium chloride of the formula:

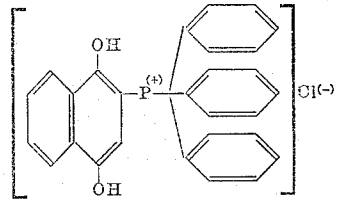


In another embodiment, the aryl nucleus Ar is a naphthalene nucleus and such compounds may be represented by the formula comprising:



wherein Z, m, R, X and n have the same meaning as above.

These compounds also all contain at least two hydroxy groups which must be in the ortho or para positions to each other. The hydroxy arrangement present may be a 1,4-dihydroxy, a 3,4-dihydroxy and the like. The polyhydroxynaphthalene group may also contain alkyl, alkoxy and halogen groups. One preferred compound of this class is 2-(1,4-dihydroxynaphthyl)-triphenyl phosphonium chloride:



The compounds of the present invention may be synthesized according to the procedures disclosed by Ramirez and Dershowitz in Journal of American Chemical Society, volume 78, pages 5614–5622 (1956). Thus, for example, there can be readily produced such compounds as 2,5-dihydroxyphenyl-triphenyl phosphonium chloride (M.P. 296.5–298.5° C.); 2-(1,4-dihydroxynaphthyl)-triphenyl phosphonium chloride (M.P. 224-227° C.); (4-chloro-2,5-dihydroxyphenyl)-triphenyl phosphonium chloride (M.P. 297–298° C.) and the like.

In addition to the above-mentioned triphenyl phosphonium chloride compounds, other such compounds can also be prepared by similar methods. For instances, halides other than the chloride, e.g., 2,5-dihydroxyphenyl-triphenyl phosphonium bromide, can be prepared. Likewise, besides having two or more hydroxy groups in the necessary positions, the aryl nucleus of such compounds may be unsubstituted, i.e., not have any other substituents, or it may be substituted by one or more substituents from the class consisting of halogen, alkyl and alkoxy groups. Halogen substituents other than chloride can be utilized. Lower alkyl groups such as methyl, ethyl, etc. and higher alkyl groups such as octyl, nonyl etc. (the latter groups being particularly useful in rendering developing agents nondiffusible), as well as alkoxy groups such as methoxy, ethoxy, etc., can be suitable substituents on the aryl nucleus.

As noted previously, the compounds of this invention are useful as photographic developing agents particularly in diffusion transfer processes. Several embodiments illustrating the use of the photographic developers of the present invention are set forth in the following nonlimiting examples.

Example 1

On a cellulose ester film support there were coated successive layers of various composition so as to form a multilayer negative or photosensitive element of the following structure:

(1) Cellulose ester film support.

(2) An emulsion layer of a red-sensitive silver iodobromide gelatin emulsion.

(3) A layer coated from a solution containing 2% cellulose acetate hydrogen phthalate and 0.75% cellulose acetate, dissolved in acetone.

(4) A layer coated from a solution containing 2% Elvanol 71–30 (trade name of Du Pont polyvinyl alcohol).

(5) An emulsion layer coated from a solution containing 7 cc. of a concentrated green-sensitive silver iodobromide gelatin emulsion, 6 cc. of water and 1 cc. of 0.5% solution of 2,5-dihydroxyphenyl-triphenyl phosphonium chloride.

(6) A layer coated from a solution containing 2% cellulose acetate hydrogen phthalate and 0.5% cellulose acetate, dissolved in acetone.

(7) A layer coated from a solution containing 1.5% Elvanol 71–30.

(8) An emulsion layer of a blue-sensitive silver iodobromide gelatin emulsion.

This negative was exposed and processed, using an aqueous solution containing 3% sodium hydroxide and 5% sodium carboxymethyl cellulose for an imbibition period of approximately three minutes against a fogged negative. The green-sensitive emulsion layer in which the 2,5-dihydroxyphenyl-triphenyl phosphonium chloride was initially located was substantially fully developed. Examination of the blue-sensitive and red-sensitive layers showed that there was very low development. The superposed fogged negative showed very little development, indicating that very little developer had migrated.

Example 2

In a silver transfer embodiment such as shown, for example, in U.S. Patent 2,662,822 and many others, incorporation of 2-(1,4-dihydroxynaphthyl)-triphenyl phosphonium chloride as the developing agent in a layer of cellulose acetate hydrogen phthalate coated on the silver halide emulsion layer resulted in substantially full development of the emulsion layer.

From examples 1 and 2 above, it is evident that the developers of the present invention are useful in systems in which the negative image is developed by a low mobility or substantially nondiffusing developing agent. Thus, the developers embodied within the present invention have particular utility in diffusion-transfer reversal processes, both dye and silver, where it is desirable to keep the developer out of the positive image or print-receiving element. It should be mentioned that with appropriate substituents, nondiffusing developers can be obtained. For instance, such developers can result by the inclusion of a hydrophobic grouping, for example, a long chain alkyl group such as octyl, on the polyhydroxy aryl grouping or nucleus.

One useful embodiment for employing the disclosed developing agents in silver diffusion transfer processes comprises developing the negative or latent image with a substantially immobile or substantially nondiffusing developing agent of the present invention, and then developing the image in transferred silver complex with a second developing agent which is a slow developer and which has little effect in developing the latent image. A developer of this latter-mentioned type is ascorbic acid which may be included in the processing composition. It should be noted that developers of this type, e.g., ascorbic acid, have little or no tendency to stain the transfer image with development oxidation products.

It will be apparent that the relative proportions of developing agents and other ingredients and materials illustrated in the above examples may be varied to suit the requirements of one skilled in the art. Thus, it is within the scope of this invention to substitute alkalies other than sodium hydroxide in the processing composition. Likewise, it is also contemplated that where desirable the processing or developing compositions may be modified by the inclusion of other common components of developer compositions such as restrainers, preservatives, accelerators, etc. Where the processing compositions are to be employed in silver diffusion transfer processes, they may have incorporated in them as a further ingredient a silver halide solvent such as sodium thiosulfate. If the processing composition is to be applied to the emulsion by being spread thereon in a thin layer, it may also include a film-forming thickening agent such, for example, as a high molecular weight polymer, sodium carboxymethyl cellulose.

Since the photographic developers of the present invention slowly revert to the intermediate quinone-phosphine adduct in alkaline solutions, it is preferable that the developer and alkaline solution be mixed or added together just prior to use. Moreover, since the disclosed developers are of low mobility and substantially nondiffusing, it is preferable, in diffusion transfer processes of the type mentioned and illustrated above, that the developing agents be incorporated in, on or behind the photosensitive silver halide emulsion and an alkaline processing composition or solution added thereto when development is desired.

In addition to being useful as silver halide developers, the triphenyl phosphonium halides described above can also be used as accelerating developers for dye developer processes such as set forth, for example, in the copending U.S. application of Howard G. Rogers, Serial No. 748,421, filed July 14, 1958, which is a continuation-in-part of Serial No. 415,073, filed March 9, 1954, now abandoned. The triphenyl phosphonium halides of the present invention can also be used in the positive or print-receiving element as nondiffusible reducing agents or antioxidants. Additionally, these compounds can be employed in appropriate interlayers of a multilayer photosensitive element useful in the production of a multicolor image so as to be a barrier for diffusing oxidized developing agent and thus help achieve reaction to take place within the proper layers of the photosensitive element as well as good color rendition.

Since certain changes may be made in the above processes, products and compositions 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. The process of developing a latent image in a silver halide emulsion which comprises treating said emulsion with an aqueous alkaline solution in the presence of a developer selected from the group consisting of compounds within the formula:

$$\left[Z_m\text{—}Ar\text{—}\overset{(+)}{P}\text{—}(R)_3 \right] X^{(-)}$$
$$\qquad\qquad\quad |$$
$$\qquad\quad (OH)_n$$

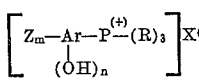
wherein Ar is an aryl nucleus selected from the group consisting of benzene and naphthalene, Z is selected from the group consisting of alkyl, alkoxy and halogen groups, *m* is an integer including zero, R is a phenyl group, *n* is at least two, and X is a halogen group, the hydroxy groups being in one of the positions ortho- and para- to each other.

2. A process of developing a latent image in a silver halide emulsion which comprises treating said emulsion with an aqueous alkaline solution in the presence of 2,5-dihydroxyphenyl-triphenyl phosphonium chloride.

3. A process of developing a latent image in a silver halide emulsion which comprises treating said emulsion with an aqueous alkaline solution in the presence of

2-(1,4-dihydroxynaphthyl)-triphenyl phosphonium chloride.

4. A photographic product comprising a plurality of layers, at least one of said layers including a silver halide emulsion, and at least one of said layers including a developing agent selected from the group consisting of compounds within the formula:



wherein Ar is an aryl nucleus selected from the group consisting of benzene and naphthalene, Z is selected from the group consisting of alkyl, alkoxy and halogen groups, m is an integer including zero, R is a phenyl group, n is at least two, and X is a halogen group, the hydroxy groups being in one of the positions ortho- and para- to each other.

5. A photographic product comprising a plurality of layers, at least one of said layers including a silver halide emulsion, and at least one of said layers including the developing agent, 2,5-dihydroxyphenyl-triphenyl phosphonium chloride.

6. A photographic product comprising a plurality of layers, at least one of said layers including a silver halide emulsion, and at least one of said layers including the developing agent, 2-(1,4-dihydroxynaphthyl)-triphenyl phosphonium chloride.

References Cited in the file of this patent

Ramirez et al.: S.A.C.S., vol. 78, pages 5614–22 (1956).