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PHOTOGRAPHIC DEVELOPER AND PROCESS

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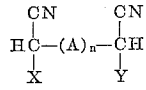
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6 Claims. (Cl. 96—66)

The present invention is concerned with a photographic developer solution and with a process for developing black and white photographic images by means of selected polycyano organic compounds as developing agents.

Developing agents are compounds which are characterized by a capacity for selectively reducing exposed silver halide in the presence of unexposed silver halide, the selectivity being of such a degree that the agent will reduce a major portion of the exposed silver halide in a photographic emulsion before any substantial amount of unexposed silver halide is reduced. In this process the developing agent becomes oxidized.

An object of this invention is to provide a new class of developer solutions which have general utility in the development of exposed silver halide. Another object is to provide such solutions which utilize available polycyano compounds. A further object is to provide such solutions which are simple to prepare and use. A still further object is to provide new processes for developing silver halide latent images.

According to the present invention there are provided new and useful developers comprising an aqueous alkaline solution having a pH greater than 7.6 and containing 0.01% to 5.0% of at least one polycyano compound of the formula:



in which A is arylene, e.g., phenylene and naphthylene; n is 0 or 1; X is —CN, —COOR, —$CONH_2$, —CONHR, —$CONR_2$, —COR, —NO_2, p-O_2N-aryl, or p-NC-aryl; Y is —COOR, —$CONH_2$, —CONHR, —$CONR_2$, —COR, —SO_2R, —NO_2, aryl, p-O_2N-aryl, p-NC-aryl, p-R_2N-aryl, —F, —Cl, —Br, —OR, —ONO_2 —OSO_2R or —OCOR, and R is hydrocarbyl, i.e., alkyl, cycloalkyl, aryl, or aralkyl hydrocarbon containing up to 18 carbon atoms. Suitable hydrocarbyl radicals include methyl ethyl, dodecyl and hexadecyl; cyclopentyl and cyclohexyl; phenyl and naphthyl; benzyl and acenaphthyl.

Developers of the above type in which n is 0 may be prepared by catalytic hydrogenation of the corresponding 1,2-dicyanoethylenes, for example, by hydrogenation of the tricyanovinyl compounds which are shown in Sausen U.S. 2,813,116 and in Heckert U.S. 2,762,810. 1,2-Dicyanovinyl compounds which may be reduced to form developers of the present invention are also shown in Heckert U.S. 2,803,640.

Developers of the above type in which A is arylene may be prepared from the corresponding 1,4-bis(cyanomethyl)-aryl compounds. For example, those in which A is phenylene may be prepared from p-xylylenedicyanide. The following reaction is illustrative.

To the alcohol-free sodium ethoxide from 12 parts of sodium is added 293 parts of ethyl carbonate, 87 parts of toluene, and 39 parts of p-xylylenedicyanide. This mixture is heated with stirring until material (mostly ethanol) begins to distill through a distilling column attached to the reactor. Toluene is added to the reaction mixture at the same rate that distillate is collected until the head temperature reaches 115° C. This process requires the addition of about 217 parts of toluene. To the cooled reaction mixture is added 300 parts of water and 42 parts of glacial acetic acid. The oil that separates is collected, and

the aqueous phase is extracted with two 71-part portions of ether. The combined oil and ether extracts are dried over magnesium sulfate and freed of volatile material by distillation at 15 mm. pressure at 80–100° C. The oil that remains is distilled, and the portion that boils at 223° C./2.7 mm. to 231° C./2.0 mm. is collected The resulting 1,4 - bis - [cyano(ethoxycarbonyl)methyl]benzene weighs 33 parts (44% yield) and crystallizes slowly to a moist solid when stored at room temperature. The infrared spectrum of the material shows bands at 4.45 microns (—C≡N) and 5.72 microns (ester >C=O). When an ethanol solution of this material is mixed with ammoniacal silver nitrate, a silver mirror forms, and the solution develops a deep blue color.

The developer solutions of this invention can be prepared by dissolving from 0.01% to 5% by weight of one or more compounds of the above formula in an aqueous medium having a pH in excess of 7.6. The desired alkalinity may be obtained by incorporating in the medium alkali metal bicarbonates, alkali metal carbonates, alkali metal hydroxides, alkali metal bisulfites, alkali metal borates, and alkali metal phosphates. Suitable specific compounds of each of these classes are the sodium and potassium compounds.

The polycyano compounds indicated above are substantially colorless. During the development of exposed silver halide or latent images the polycyano compounds are oxidized. In the first step of oxidation, two hydrogen atoms are removed and a unit of carbon-to-carbon unsaturation is introduced into the molecule. Some of the resulting oxidized compounds, however, are colored. When such a colored compound is formed, it normally remains adjacent to the reduced silver which caused it to form and thereby intensifies the developed image. Where desired, such color may be removed by selective solvent extraction or by chemical bleaching, such as by strong alkali or sulfite.

The development of exposed silver halide images in photographic films and papers may be carried out over the full temperature range of liquid aqueous systems, i.e., from about 0° C. to about 100° C. However, many photographic elements are injured by hot water, and temperatures in the range of about 10–45° C. are preferred. Pressure is not a factor in this process, and ordinary atmospheric pressure is accordingly preferred.

The invention will be further illustrated by, but is not limited to, the following examples wherein the parts are by weight unless otherwise indicated.

EXAMPLE I

A photographic developer is prepared by dissolving two parts of 1,2-dicyano-1,2-dicarbethoxyethane (Felton and Orr, J. Chem. Soc., 1955, 2170), two parts of potassium bromide, 10 parts of sodium bicarbonate, and 20 parts of sodium carbonate in 1000 parts of water. One end of a strip of a commercial positive film having a light-sensitive gelatino-silver halide emulsion layer is exposed to light through a stepwedge while protecting the remaining area from the light. In a photographic darkroom the exposed film is immersed in the above developer solution at 72° F. for 12 minutes. The developer solution remains essentially colorless and there is no staining of the film. The film is then fixed in hypo and washed by conventional photographic procedures. The exposed area of the film contains a well-graded image of the stepwedge. In the step of maximum exposure, the optical density is 1.6. In the unexposed area, examined for fog, the density is 0.06, of which at least 0.03 is due to the film base.

The superiority of the developers of this invention over tetracyanoethane is illustrated by comparing the above results with the following:

A developer solution is prepared exactly as above ex-

cept that two parts of tetracyanoethane is employed in place of the 1,2-dicyano-1,2-dicarbethoxyethane. An identically exposed strip of commercial positive film is developed in this solution at 72° F. Development is stopped after one minute, due to fogging. After fixing and washing as above, the film is examined for optical density. In the area of maximum exposure the density is 0.92. In the unexposed area the density is 0.29 and this area is visibly strongly fogged. Prolonging development time to increase the maximum exposed area from a density of 0.92 to a density of 1.6, as above, would obviously still further increase the fogging of unexposed areas.

EXAMPLE II

Part A

A solution of 233 parts of potassium cyanide in 700 parts of water is added to a mixture of 310 parts of alpha-cyano-beta-phenylpropionamide [Day and Thorpe, J. Chem. Soc., 117, 1473 (1920)] and 533 parts of ethanol. The resulting mixture is stirred until dissolved and 525 parts of glacial acetic acid is then added. When this solution is diluted with 5000 parts of water, an oil separates. This oil solidifies and the solid is recrystallized from aqueous ethanol to yield 199 parts (55% yield) of alpha, beta-dicyano-beta-phenylpropionamide melting at 174.5–177° C.

Part B

A photographic developer solution is prepared by dissolving 3 parts of alpha, beta-dicyano-beta-phenylpropionamide in 1000 parts of 5% aqueous sodium carbonate (pH 11.2). An area near one end of a commercial positive photographic film having a light-sensitive, gelatino-silver halide emulsion layer is exposed to light while protecting the remaining area from the light. In a photographic dark room the partly exposed film is immersed in the above developer solution at 72° F. for 15 minutes. It is then fixed in hypo and washed by conventional photographic procedures. The exposed area of the film contains dark developed-silver and the unexposed area is essentially clear, there being a sharp, visible demarcation between the exposed and unexposed areas of the film.

EXAMPLE III

A photographic developer solution is prepared by dissolving 3 parts of alpha, beta, beta-tricyanoethylbenzene [Corson and Stoughton, J. Am. Chem. Soc., 50 2825–37 (1928)] in 1000 parts of 5% aqueous sodium carbonate (pH 11.2). An area near one end of a commercial positive photographic film is exposed to light while the remaining area is protected from the light. In a photographic dark room the partly exposed film is immersed in the above developer solution at 72° F. for 150 minutes. It is then fixed in hypo and washed by conventional photographic procedures. The exposed area of the film contains dark developed-silver and the unexposed area is essentially clear, there being a sharp, visible demarcation between the exposed and unexposed areas of the film.

EXAMPLE IV

A photographic developer solution is prepared by dissolving 3 parts of N,N-dimethyl-p-(alpha, beta, beta-tricyanoethyl)-aniline [McKusick et al., J. Am. Chem. Soc., 80, 2809 (1958)] in 1000 parts of 5% aqueous sodium carbonate (pH 11.2). An area near one end of a commercial positive photographic film having a light-sensitive, gelatino-silver halide emulsion layer is exposed to light. In a photographic dark room the partly exposed film is immersed in the above developer solution at 72° F. for 150 minutes. It is then fixed in hypo and washed by conventional photographic procedures. The exposed area of the film contains dark developed-silver while the unexposed area is clear, there being a sharp, visible demarcation between the exposed and unexposed areas of the film.

Other specific polycyano developing agents which may be used in the processes of this invention, i.e., substituted for 1,2-dicyano-1,2-dicarbethoxyethane in Example I, include the following:

p-Bis(1-cyano-1-ethoxycarbonylmethyl)benzene
p-Bis(1-cyano-1-allyloxycarbonylmethyl)benzene
2,3-diacetylsuccinonitrile
2-(p-nitrophenyl)-3-(N-phenylcarbamyl)succinonitrile
2-(p-cyanophenyl)-3-(N-cyclohexyl-N-stearylcarbamyl)-succinonitrile
2-(N-cyclohexyl - N - stearylcarbamyl) - 3 - (p-tolylsulfonyl)-succinonitrile
1,4-bis(cyanonitromethyl)naphthalene
9,10-dihydro-9,10-bis(alpha,p-dicyanobenzyl)anthrecene
2-chloro-3-phenylsulfonylsuccinonitrile
2,N,N-dodecylcarbamyl-3-fluorosuccinonitrile
2-bromo-3-nitrosuccinonitrile
1,1,2-tricyanoethyl nitrate
1,1,2-tricyanoethyl benzenesulfonate
1,2-dicyano-2-(N-ethylcarbamyl)ethyl acetate
1,2-dicyano-2-(N-decylcarbamyl)ethyl t-butyl ether
2,3-dicarbamylsuccinonitrile
2-(benzyloxycarbonyl) - 3 - (p-dimethylaminophenyl)-succinonitrile

Mixtures of two or more of the specific polycyano compounds set forth above and in the examples can be used in the developer solutions of this invention.

The developer solutions of this invention can contain, in addition to the novel polycyano compounds of the general formula given above, various other adjuvants such as restrainers, e.g., potassium bromide; antioxidants, e.g., sodium and potassium sulfite; accelerators, e.g., polyethylene oxides; antifoggants, e.g., 6-nitrobenzimidazole and benzotriazole; sequestering agents, e.g., of the aminoacetic acid type. The polycyano compounds can be used in combination with other photographic developing agents, e.g., metol, hydroquinone, phenidone and other conventional developing agents.

The novel developer solutions can also be used in inverse-transfer and stabilization processes with conventional steps using silver halide solvents.

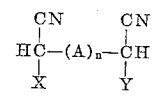
The invention is not limited to the development of any particular type of photographic film and can be used in developing X-ray film, black and white motion picture film, lithographic film, and portrait film. It is also useful in developing photographic papers of various types.

The films and papers may contain various types of light-sensitive silver halide dispersed in a water-permeable binder. Thus, the silver halide can be silver chloride, silver bromide, silver bromochloride, silver iodobromide or mixtures of these. The binding agent can be gelatin or other natural protein colloids, e.g., zein, casein and alubumin, or a synthetic colloid having protective colloid properties, e.g., polyvinyl alcohol, polyvinyl acetals and the addition polymers described in Shacklett U.S. Patent 2,833,650.

An advantage of the invention is that it is simple and gives dependable results. It provides new developers of general utility for the formation of developed silver images. The agents do not have any adverse physiological effect on the average person during normal use.

What is claimed is:

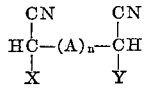
1. A process for reducing an exposed silver halide to silver which comprises subjecting said silver halide to the action of a developer solution comprising an aqueous alkaline solution having a pH greater than 7.6 and containing from 0.01% to 5.0% by weight of at least one polycyano compound of the formula



wherein A is a member taken from the group consisting of phenylene and naphthylene, *n* is a cardinal number

taken from the group 0 and 1, X is a member taken from the class consisting of —CN, —COOR, —$CONH_2$, —CONHR, —$CONR_2$, —COR, —NO_2, p-O_2N-phenyl, and p-NC-phenyl, and Y is a member taken from the class consisting of —COOR, —$CONH_2$, —CONHR, —$CONR_2$, —COR, —SO_2R, —NO_2, phenyl, p-O_2N-phenyl, p-NC-phenyl, p-R_2N-phenyl, —F, —Cl, —Br, —OR, —ONO_2, —OSO_2R, and —OCOR, and wherein R is a hydrocarbyl radical of 1 to 18 carbon atoms.

2. A process for developing an exposed silver halide emulsion layer comprising treating said emulsion layer with an aqueous alkaline solution having a pH greater than 7.6 and containing from 0.01% to 5.0% by weight of at least one polycyano compound of the formula



wherein A is a member taken from the group consisting of phenylene and naphthylene, *n* is a cardinal number taken from the group 0 and 1, X is a member taken from the class consisting of —CN, —COOR, —$CONH_2$, —CONHR, —$CONR_2$, —COR, —NO_2, p-O_2N-phenyl and p-NC-phenyl, and Y is a member taken from the class consisting of —COOR, —$CONH_2$, —CONHR, —$CONR_2$, —COR, —SO_2R, —NO_2, phenyl, p-O_2N-phenyl, p-NC-phenyl p-R_2N-phenyl, —F, —Cl, —Br, —OR, —ONO_2, —OSO_2R, and —OCOR, and wherein R is a hydrocarbyl radical of 1 to 18 carbon atoms, and removing the unexposed and undeveloped silver halide.

3. A process as defined in claim 1 wherein said polycyano compound is alpha, beta-dicyano-beta-phenylpropionamide.

4. A process as defined in claim 1 wherein said polycyano compound is alpha, beta, beta-tricyano-ethylbenzene.

5. A process as defined in claim 1 wherein said polycyano compound is N,N-dimethyl-p-(alpha, beta, beta-tricyanoethyl)-aniline.

6. A process as defined in claim 1 wherein said polycyano compound is 1,2-dicyano-1,2-dicarbethoxyethane.

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McKusick et al.: J. Am. Chem. Soc., 80, 2809 (1958).