United States Patent Office 3,053,656 Patented Sept. 11, 1962

3,053,656

PHOTOGRAPHIC SILVER HALIDE DEVELOPERS CONTAINING TRIAZINE RINGS

Richard S. Corley, Wellesley Hills, Mass., assignor to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware

No Drawing. Filed Dec. 17, 1958, Ser. No. 780,964
13 Claims. (Cl. 96—29)

This invention relates to photography and more particularly to compositions and processes for development of photosensitive silver halide elements.

One object of the present invention is to provide novel processes and compositions for the development of latent images present in photosensitive silver halide emulsions.

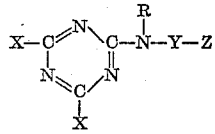
A further object of the present invention is to provide novel compounds which are capable of developing exposed silver halide emulsions.

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

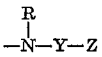
The invention accordingly comprises the several steps and the relation and order of one or more such steps with respect to each of the others, and the products and compositions possessing the features, properties and relation of elements which are exemplified in the following detailed disclosure, and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

A novel class of photographic developing agents has been discovered, these compound corresponding to the formula:

(A)

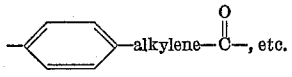


wherein X is selected from the group consisting of

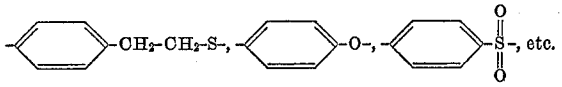


chloro, hydroxyl, alkyl, amino, aminoalkyl, aryloxy, and alkoxy radicals; R is hydrogen or an alkyl group; Y is a divalent radical or a covalent bond; and Z is an aryl nucleus selected from the group consisting of benzene and naphthalene nuclei substituted by at least two members of the group consisting of hydroxyl and amino groups so as to be capable of developing a silver halide latent image.

As examples of divalent radicals, signified by the term "Y" in Formula A and suitable for use in the practice of the present invention, mention may be made of: divalent organic radicals such as alkylene radicals, preferably lower alkylene radicals such as ethylene, isopropylene, etc.; arylene radicals such as phenylene, etc.; aralkylene radicals such as phenethyl, etc.; acyl radicals such as



and organic radicals which contain both hetero and carbon atoms as constituent components, as for example,



The novel compounds of this invention, as noted above,

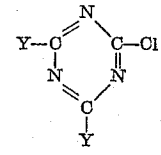
are silver halide developing agents which contain an aryl nucleus selected from the group consisting of benzene and naphthalene nuclei so substituted by at least two groups selected from the group consisting of hydroxyl and amino groups as to be capable of developing an exposed silver halide emulsion. A preferred silver halide developing group comprises a hydroquinonyl group. Other suitable developing groups include ortho-dihydroxyphenyl, triaminophenyl, ortho- and para-amino substituted hydroxyphenyl groups, and the corresponding naphthalene developing groups. In general, the developing group comprises a benzenoid developing configuration, that is, an aromatic developing group which forms quinonoid or quinone products upon oxidation.

In addition to the substituents which provide the silver halide developing function, Z may be substituted by halogen, alkoxy, alkyl, etc., radicals. The term "amino" as used herein is intended to include amino groups so substituted as not to impair their respective silver halide developing functions, for example, suitably substituted alkylamino and arylamino groups.

Examples of specific triazine photographic developing agents within the scope of the above formula include hydroquinoneamino-dihydroxy - s - triazine, 2-hydroquinoneamino-4-chloro-6-hydroxy-s-triazine, and 2,4-bis-(hydroquinoneamino)-6-hydroxy-s-triazine.

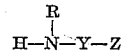
The developing agents of this invention may be prepared by reacting a triazine compound of the formula:

(B)



wherein Y is selected from the group consisting of chloro, hydroxyl, alkyl, amino, aminoalkyl, aryloxy, and alkoxy radicals; with a compound of the formula:

(C)



wherein R, Y and Z have the same significance as in Formula (A); such as

Amino-phenethyl-hydroquinone, the preparation of which is disclosed in the copending U.S. application of Elkan R. Blout, Milton Green, Howard G. Rogers, Myron S. Simon and Robert B. Woodward, Serial No. 612,051, filed September 25, 1956;

Amino-phenethyl-thio-hydroquinone, the preparation of which is disclosed in the copending U.S. application of Milton Green and Howard G. Rogers, Serial No. 663,876, filed June 6, 1957, now U.S. Patent No. 3,009,958, issued November 21, 1961;

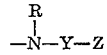
Amino-phenoxy-hydroquinone, the preparation of which is disclosed in the copending U.S. application of Milton Green and Warren E. Solodar, Serial No. 680,406, filed August 26, 1957;

Amino-propyl-amino-hydroquinone, the preparation of which is disclosed in the copending U.S. application of Milton Green and Myron S. Simon, Serial No. 711,812, filed January 29, 1958, now Patent No. 3,002,997 issued October 3, 1961; and

Amino-hydroquinone, amino-ethyl-hydroquinone, amino-phenyl-hydroquinone, and amino-phenyl-sulfonyl-hy-

droquinone, etc., which may be prepared by known chemical reactions;

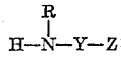
in an inert organic reaction medium, such as acetone or pyridine. The amine is employed in the ratio of approximately one mole, per mole of triazine compound, for each



group to be introduced. Reaction with the triazine compound proceeds roughly stepwise; for example, with cyanuric chloride, the first chlorine reacts at temperatures of about —10° C. to about 0° C., the second chlorine at about 40 to 50° C. and the third chlorine at about 90 to 100° C. Thus, it will be apparent to one skilled in the art that this provides an effective means of controlling the degree and nature of substitution of the triazine ring, thereby enabling him to obtain developing agents of varying developing potential within the scope of this invention.

It is generally desirable to protect the hydroxyl and/or amino groups of the developing function, during reaction, to avoid undesirable side reactions, for example, to employ a protected derivative of Z, that is, a compound within the formula:

(D)



wherein R and Y have the same significance as previously stated and Z^1 represents the protected derivatives of a benzenoid silver halide developing group selected from the group consisting of benzene and naphthalene nuclei so substituted by at least two groups selected from the group consisting of hydroxyl and amino groups as to be capable of developing an exposed silver halide emulsion, as for example, the ester derivatives thereof.

The compounds of Formula D may be prepared, for example, by the esterification of the compounds of Formula C.

After reaction and prior to use as a photographic developing agent, the ester groups may be removed by deesterification, as for example, by hydrolysis in the presence of alkali.

An example of one method of preparing the novel developing agents of this invention and set out by way of illustration only is the following:

Example 1

A solution of 16.2 g. of cyanuric chloride in 35–40 cc. of boiling acetone is poured slowly, with vigorous mechanical stirring, into 400 cc. of water kept at 0° C. in a flask submerged in an ice-bath, and 20 g. of 2-aminohydroquinone-4-benzoate in concentrated solution in 35–40 cc. of boiling acetone is poured in. A solution of 7.5 g. of sodium bicarbonate in 50 cc. of water is then added over a period of about 10–15 minutes. The mixture is stirred for about 15–30 minutes, at which point the pH should be about 5–6. The mixture is then filtered, the filter cake is pressed dry and then washed with water. The washed filter cake is dried in a vacuum desiccator over concentrated sulphuric acid. The dry product is washed by trituration three times with 25–35 cc. portions of boiling ether, filtered and dried.

Average yields of 90 to 95% were obtained in several runs performed as described. The crude O-monobenzoyl hydroquinoneamino-dichloro-s-triazine product melts, with decomposition, at about 220–223° C. and at 225° C. when pure. It is soluble in acetone and aqueous alkali, insoluble in water, and very slightly soluble in ether. Analysis of the product shows:

	Calculated for $C_{16}H_{10}O_3N_4Cl_2$	Found
C	50.9	51.0
H	2.67	2.8
N	14.8	14.5
Cl	18.8	18.5

The crude product may be hydrolyzed by heating, under nitrogen, for about 15 minutes at 100° C. in excess 5% alkali. The hydrolyzed product may be precipitated in acid, yielding a tan powder. On recrystallization from methanol, a pink tan powder is obtained which melts at about 310° C., is soluble in alkali, sparingly soluble in methanol, and insoluble in water and acetone.

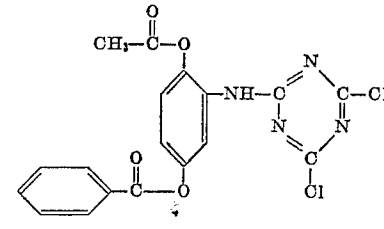
Example 2

The bis-substituted triazine compound may be prepared by dispersing monobenzoyl hydroquinone-amino cyanuryl dichloride, for example the unfiltered reaction mixture of Example 1 having a pH of 5–6, in water at 40–50° C. A solution of 20 g. of 2-amino-hydroquinone-4-benzoate in boiling acetone is then added. A solution of 4.67 g. of anhydrous sodium carbonate in 20 cc. of water is added over a period of one hour and the mixture stirred an additional hour at 45–50° C. The crude reaction product may be worked up in the same manner as described in Example 1. The crude product is insoluble in acetone and hot organic solvents, such as pyridine, ethanol and nitrobenzene. The crude bis-product may be hydrolyzed by heating under nitrogen, in warm alkali for about 10 minutes to give an alkali-soluble hydrolysis product, 2,4-bis-(hydroquinoneamino)-6-hydroxy-s-triazine.

In certain instances, as where these novel triazine compounds are used as intermediates, as for example, for other photographic compounds, it may be desirable to have one or both hydroxyl groups in the developing function esterified to avoid or reduce side reactions. After reaction the free hydroxyl groups are regenerated by hydrolysis of the product. Amino groups in the developing function may be similarly protected. An example of such a protected triazine compound is:

Example 3

Ten grams of O-monobenzoyl hydroquinoneamino-dichloro-s-triazine is suspended in 35–50 cc. of acetic anhydride and warmed on a steam bath. Concentrated sulfuric acid is added drop by drop until solution is obtained (5 to 10 drops), following which the desired product crystallizes out as fine needles. The reaction mixture is chilled and filtered. The solid material recovered is washed with cold water and then with a little 1:1 acetone and water. The crude product (9.8 g., 88% yield, M.P. 205–6° C.) is recrystallized from acetone. Two crops of crystals give a 96% recovery of O,O-acetyl benzoyl hydroquinoneamino-dichloro-s-triazine of the structure:



having a melting point of 210° C. The product is insoluble in water and cold alkali, very slightly soluble in ether and cold acetone and moderately soluble in hot acetone. Analysis of the product shows:

	Calculated	Found
C	51.7	52.0
H	2.88	2.9
Cl	17.0	17.1

The novel triazine developing agents of this invention may be used in conventional multistage and multibath photographic processing procedures in either black-and-white or color photography. They are also useful as de-

veloping agents 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. Example of such processes are disclosed in U.S. Patent 2,647,056 to Edwin H. Land.

As noted above, the herein disclosed novel triazine developing agents are useful in transfer processes of the type disclosed in the said patent to Edwin H. Land, and in other processes in which the problem of a residual stain cannot be readily met by washing operations. When used for transfer purposes, the novel developer compositions of this invention have incorporated therein as a further ingredient a silver halide solvent, such as sodium thiosulfate. If the 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 the high molecular weight polymer, sodium carboxymethyl cellulose. Experience has shown that concentrations of about 3%, by weight, of these novel triazine developing agents, for example hydroquinoneamino-dihydroxy-s-triazine, will give good results in the above described transfer processes.

It will be apparent that the relative proportions of the developer set forth above may be varied to suit the requirements of the operator. Thus, it is within the scope of this invention to combine the aforementioned developing agent with suitable preservatives, alkalies, 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.

The developing agent may be disposed prior to exposure in a photosensitive element comprising the photographic emulsion, and the developer composition containing the agent formed by permeating the emulsion with an aqueous alkaline liquid capable of solubilizing the agent. Where desired, the developing agent may be dissolved in an aqueous alkaline solution prior to application thereof to an exposed silver halide emulsion.

Particularly useful developer compositions may also contain an auxiliary or accelerating developer such as metol, benzylaminophenol or a 3-pyrazolidone such as 1-phenyl-3-pyrazolidone.

It will be apparent that the triazine developing agents of this invention may also be used in conventional black-and-white tank and tray development.

The triazine developers of this invention are very stable to heat and light. For example, the novel triazine derivatives of aminohydroquinone of this invention are much more stable than aminohydroquinone itself, and this is an important advantage in the use of these triazine compounds.

One further and very important advantage in the use of the novel triazine compounds of this invention must be noted. Aminohydroquinone is a non-discriminatory developing agent and is therefore of little photographic value. On the other hand, the novel triazine derivatives of aminohydroquinone disclosed herein are very discriminatory in their developing action and they are therefore highly useful as photographic developing agents.

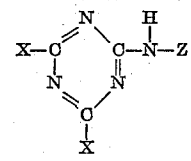
The present application is a continuation-in-part of my copending application Serial No. 440,855, filed July 1, 1954, now abandoned.

Since certain changes may be made in the above product and process 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 alkaline solution containing a silver halide

solvent and at least one compound of the formula:



wherein each X is selected from the group consisting of chloro, hydroxyl and



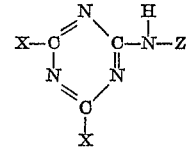
radicals, and Z is a dihydroxyphenyl silver halide developing radical.

2. A photographic developer composition as defined in claim 1, wherein said compound is hydroquinoneamino-dihydroxy-s-triazine.

3. A novel photographic developer composition as defined in claim 1, wherein said compound is 2-hydroquinoneamino-4-chloro-6-hydroxy-s-triazine.

4. A novel photographic developer composition as defined in claim 1, wherein said compound is 2,4-bis-(hydroquinoneamino)-6-hydroxy-s-triazine.

5. The process of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion with an aqueous alkaline solution of a silver halide developing agent of the formula:



wherein each X is selected from the group consisting of chloro, hydroxyl and



radicals, and Z is a dihydroxyphenyl silver halide developing radical.

6. A process as defined in claim 5 wherein said silver halide developing agent is hydroquinoneamino-dihydroxy-s-triazine.

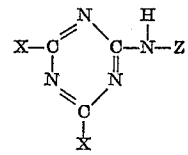
7. The process as defined in claim 5, wherein said compound is 2-hydroquinoneamino - 4 - chloro - 6 - hydroxy-s-triazine.

8. The process as defined in claim 5, wherein said compound is 2,4 - bis - (hydroquinoneamino) - 6 - hydroxy-s-triazine.

9. A process as defined in claim 5 wherein said compound is disposed, prior to exposure, in a photosensitive element comprising said photographic emulsion and the solution containing said compound is formed by permeating said emulsion with an aqueous alkaline liquid capable of solubilizing said compound.

10. A process as defined in claim 5 wherein said compound is dissolved in an aqueous alkaline solution prior to application thereof to said exposed emulsion.

11. The process which comprises developing an exposed silver halide emulsion with an aqueous alkaline solution containing a silver halide solvent and at least one compound of the formula:



wherein each X is selected from the group consisting of chloro, hydroxyl and



radicals, R is a hydrogen atom and Z is a dihydroxyphenyl silver halide developing radical; contacting unexposed and undeveloped silver halide therein with said silver halide solvent and forming thereby an imagewise distribution of a soluble silver complex in the undeveloped areas of said emulsion; and transferring by imbibition, at least in part, said imagewise distribution of soluble silver complex to a superposed image-receiving layer to provide a silver transfer image.

12. A process as defined in claim 11 wherein said compound is hydroquinoneamino-dihydroxy-s-triazine.

13. The process as defined in claim 11 wherein



comprises a hydroquinonealkyleneamino group.

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