United States Patent Office

3,305,363

Patented Feb. 21, 1967

3,305,363

PHOTOGRAPHIC DEVELOPMENT PROMOTERS

Dorothy J. Beavers and Norman Allentoff, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

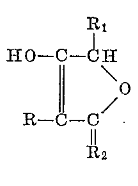
No Drawing. Filed Nov. 13, 1962, Ser. No. 237,382
6 Claims. (Cl. 96—66.3)

This invention relates to photography. In particular, it relates to use of certain compounds as development promoters with photographic developers.

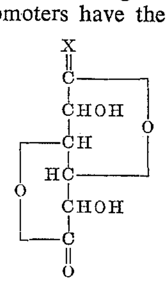
An object of the invention is to provide a new use for compounds as development promoters in photographic development proceses. One specific object is to provide photographic silver halide emulsions having incorporated therein compounds that will act as development promoters when placed in alkaline solution in the presence of an organic silver halide developer.

Use of enediol lactone compounds as agents for silver halide development is known (see, for example, U.S. Patents 2,688,548 and 2,688,549 to Reynolds et al.). The present invention provides compounds that have an accelerating or super-additive effect when used with silver halide developers, similar to the effect of enediol lactones but that have no independent developing activity. Instead of the characteristic active enediol group of enediol lactone class of promoters, the present compounds have a less active enol group.

Specifically, compounds useful according to the present invention as development promoters have the formulas:



and



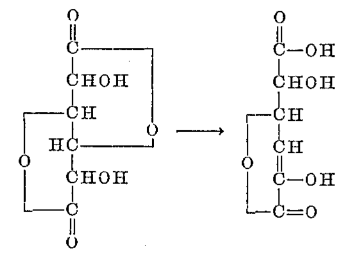
I II

wherein R is a member selected from the group consisting of H, Cl, and Br, R_1 is a member selected from the group consisting of H, alkyl containing 1–5 carbon atoms and aryl, R_2 is a member selected from the group consisting of oxo and imino, and X is a member selected from the group consisting of oxo and [—H, —OH].

Enol lactones and dilactones of the class described are stable against oxidation when included in photographic silver halide emulsions which are acid. Such stability is an advantage not possessed by the enediol lactones. These stable promoters can be incorporated in acid silver halide emulsions with stable developers such as phenidone and the like. Specific examples of enediol lactones having the Formula I above are

(1) Tetronic acid—I, R=H, R_1=H, R_2=oxo
(2) α-Bromotetronic acid—I, R=Br, R_1=H, R_2=oxo
(3) α-Chlorotetronic acid—I, R=Cl, R_1=H, R_2=oxo

Dilactones of Formula II above are not enol lactones, but can be considered equivalent in the present invention because they are stable in acid silver halide emulsions and they hydrolyze in alkaline solution, e.g. developer solution, to form an active enol lactone, e.g.



Specific examples of dilactones that are useful according to the invention are D-mannosaccharo-1,4:3,6-dilactone (II, X=oxo) and D-glucuronolactone (II, X=[—H, —OH]). The latter is commercially available.

Unlike enediol lactones, these enol lactones show very little or no photographic developing action, even though they may retain some reducing activity as with Fehling solution. However, when these compounds are added to a developing solution containing a developer such as a 1-phenyl-3-pyrazolidone for example, or are incorporated in a silver halide emulsion which is eventually treated with a developing solution containing an organic developer, an acceleration or superadditive action is produced by means of the enol lactones. Compounds of the class described are useful as promoters in processes for silver halide development which comprise the step of washing an exposed film of silver halide emulsion with an alkaline solution in the presence of an organic silver halide developer and a promoter of the class described. Preferably the promoter is included in the photographic emulsion, as is described in the examples below, but our invention also includes processes in which a promoter of the class described is added directly in the alkaline developer solution. Although it is usually preferred to have one developer incorporated in the emulsion and a second developer in the alkaline solution as in the examples below, our invention includes processes in which all of the developer is incorporated in the emulsion and processes in which all of the developer is in the alkaline solution.

Alpha-bromotetronic acid and α-chlorotetronic acid were prepared by the method described at J. Am. Chem. Soc., 60, 857–864 (1938).

Tetronic acid was prepared as follows. To a solution of 20 grams of α-bromotetronic acid in 120 ml. of methanol was added 9.5 g. of anhydrous barium hydroxide. The mixture was hydrogenated in a Parr apparatus at 50 p.s.i. using 2.5 g. of palladium-charcoal catalyst. The hydrogenation was complete in about 15 minutes, at the end of which time all of the barium hydroxide had dissolved. The solution was filtered and evaporated to dryness in vacuum at room temperature. The residue was dissolved in a mixture of 25 ml. of water and 50 ml. of ether. The ether layer was separated and the aqueous phase was extracted with four 50-ml. portions of ether. The combined ether solution was dried with anhydrous sodium sulphate and evaporated. A yield of 9.7 g. (87%) of crude tetronic acid was obtained. This was recrystallized from a mixture of absolute ethanol and ligroin giving a product melting at 142–143° C. with decomposition.

D-mannosaccharo-1,4:3,6-dilactone was prepared as follows. A solution of 103 g. of D-mannose in 350 ml. of 1:1 by volume concentrated nitric acid and water was heated in a circulating water bath at 60° C. for 5 hours. During this time a vigorous reaction took place with evolution of nitrous oxide fumes. The solution was then heated in a bath at 85° C. for one hour and evaporated in a shallow dish at about 90° C. while being stirred with a strong jet of air. The residue was removed and dried overnight in a vacuum desiccator over solid sodium hydroxide. It was then taken up in a mixture of 50 ml. of warm water and 200 ml. of absolute ethanol. On cooling, 32 g. of crude lactone was obtained by crystallization. This was recrystallized from absolute ethanol (37.5 volumes) to give 21.4 g. of purified lactone melting at 196° C. An additional 6.5 g. of crude lactone was obtained by concentration of the original mother liquors and crystallization from ethanol.

Following are specific examples that describe preferred embodiments of the invention.

Example I

A conventional negative speed silver bromo-iodide emulsion was prepared for coating. The emulsion was divided into aliquot portions and solutions of the addenda shown in Table I were added to each portion just before coating. A portion of each preparation was coated by a conventional coating method on light weight paper stock (not baryta coated) in an amount equivalent to 150 mg. of silver per square foot and dried. After sensitometric exposure the papers were developed for 25

seconds at 32° C. in Kodak D–19–b developer having the following formula:

	Grams
Elon	2.2
Hydroquinone	8.8
Sodium sulfite (anhydrous)	72.0
Sodium carbonate (anhydrous)	48.0
Potassium bromide	4.0
Water to 1 liter.	

After development the papers were fixed, washed and dried. Relative speed was measured at reflection densities of 0.1 above fog. The effects of the addenda on fog, speed D_{max} and stability of the emulsion are shown in the following table. Also shown is the fog density found in a sample of each coated paper after incubation of the coated paper for eight days at 120° F., 35° relative humidity.

TABLE I

Addenda	Addenda, gm./gm. mol. AgX	Fog		Relative speed, 0.1 above fog	Reflection, D_{max}	Contrast above fog
		Fresh	After 8 day incuba.			
Control		0.02	0.02	100	1.18	0.79
1-phenyl-3-pyrazolidone	20	0.03	0.38	182	1.22	0.92
Ascorbic acid	80	0.32	0.83	115	1.21	0.60–0.70
1-phenyl-3-pyrazolidone plus ascorbic acid	20 80	0.17	0.83	200	1.23	0.90
1-phenyl-3-pyrazolidone plus D-mannosaccharodilactone	20 80	0.01	0.06	240	1.18	1.10
1-phenyl-3-pyrazolidone plus α-bromotetronic acid	20 80	0.09	0.02	229	1.20	0.90

Example II

A conventional negative speed silver bromoiodide photographic emulsion was prepared as in Example I with the addenda shown in Table II and tested as in Example I. Results are shown in Table II.

TABLE II

Addenda	Addenda, g./m. AgX	Fog		Relative speed, 0.1 above fog	Reflection, D_{max}	Contrast above fog
		Fresh	8 day incuba.			
Control		0.01	0.02	100	1.16	0.77
1-phenyl-4-methyl-3-pyrazolidone	20	0.01	0.50	166	1.20	0.98
1-phenyl-4-methyl-3-pyrazolidone plus glucurono lactone [1]	20 50	0.02	0.04	190	1.22	1.11

[1] Shoulder speed very high. Better incubation characteristics than control or 1-pheny-4-methyl-3-pyrazolidone alone.

Example III

A conventional negative speed silver bromoiodide photographic emulsion was coated on lightweight paper stock with the addenda shown in Table III and tested in the manner indicated in Example I. Effects of the addenda are shown in Table III.

TABLE III

Addenda	Addenda, gm./gm. mol. AgX	Fog		Relative Speed, 0.1 above fog	Reflection, D_{max}	Contrast above fog
		Fresh	8 day Incuba.			
Control		0.01	0.02	100	1.14	0.96
1-phenyl-3-pyrazolidone	20	0.04	0.09	204	1.20	1.20
1-phenyl-3-pyrazolidone plus D-mannosaccharodilactone	20 40	0.05	0.24	263	1.22	1.38
Do	20 80	0.04	0.25	302	1.22	1.29

As indicated by data in Tables I, II, and III, the presence of a promotor of the class described increases the speed and contrast of emulsions in which it is incorporated.

Some examples of stable organic silver halide developers suitable for incorporation in silver halide emulsions instead of those mentioned in the examples are 3-pyrazolidone developers such as those described in U.S. Patent No. 2,685,515 and other developers that are inactive and stable in neutral or acid emulsions.

Some examples of organic silver halide developers for use in the alkaline wash solution instead of those mentioned in the examples are: Elon-hydroquinone, hydroquinone-ascorbic acid, hydroquinone, various 3-pyrazolidone developers, and the like. When an organic developer is incorporated in the emulsion the alkaline wash may consist simply of an alkaline solution, such as a solution of an alkali metal hydroxide or carbonate and the like.

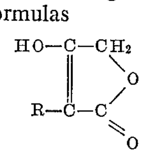
Beyond the requirement that a silver halide emulsion must be acid to be compatible with incorporated promoters, the emulsion composition is not a critical factor of the invention; any conventional acid silver halide emulsion that is useful for photographic film may be used within the scope of the present invention.

When the promoter is incorporated in a silver halide emulsion, the optimum concentration of promoter for best results usually will be in the range from 10 to 200 grams per gram mole of silver halide, and in most cases from 40 to 80 grams per gram mole.

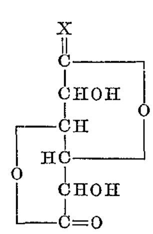
The invention has been described with reference to certain preferred embodiments and it will be understood that modifications and variations may be made within the scope of the invention as described above and as defined in the following claims.

We claim:

1. A process of developing a latent image in an exposed photographic silver halide film, comprising washing the exposed film with an alkaline solution in the presence of at least one organic silver halide developer and a promoter selected from the group consisting of compounds having the formulas



and



wherein R represents a member selected from the group consisting of H, Cl, and Br and X represents a member selected from the group consisting of oxo and

[—H, —OH]

2. The process of claim 1 wherein said alkaline soluiton contains an organic silver halide developer.

3. The process of claim 1 wherein one stable organic developer and the promoter are ingredients incorporated in the silver halide emulsion.

4. The process of claim 3 wherein said alkaline solution contains a second developer in addition to the developer incorporated in the emulsion.

5. An acid photographic silver halide emulsion having incorporated therein a stable silver halide developer and a promoter selected from the group consisting of

Tetronic acid
α-chlorotetronic acid
α-bromotetronic acid
D-mannosaccharo-1,4:3,6-dilactone
D-glucuronolactone

6. An acid photographic silver halide emulsion having incorporated therein a stable organic silver halide developer and from 10 to 200 grams of promoter per gram mole of silver halide present, said promoter being a member selected from the group consisting of

Tetronic acid
α-chlorotetronic acid
α-bromotetronic acid
D-mannosaccharo-1,4:3,6-dilactone
D-glucuronolactone

References Cited by the Examiner

UNITED STATES PATENTS

2,415,666	2/1947	Weissberger et al.	99—66
2,845,349	7/1958	Schwarz	99—66
3,022,168	2/1962	Stjarnkvist	99—66

OTHER REFERENCES

Micheel et al.: Berichte, vol. 67, pp. 1660–64 (1934).

James: Journal Photographic Science, vol. 6, pages 49–56 (1958).

NORMAN G. TORCHIN, *Primary Examiner.*

ABRAHAM H. WINKELSTEIN, *Examiner.*

J. T. BROWN, C. E. DAVIS, *Assistant Examiners.*