

Sept. 9, 1941.

G. P. HAM ET AL
PHOTOGRAPHIC DEVELOPER

2,255,731

Filed March 15, 1940

2 Sheets-Sheet 1

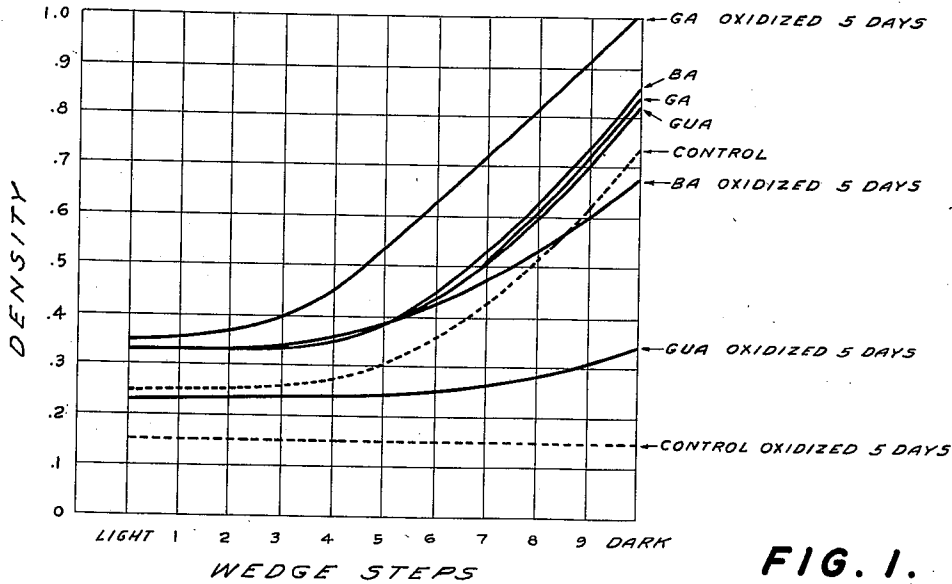


FIG. 1.

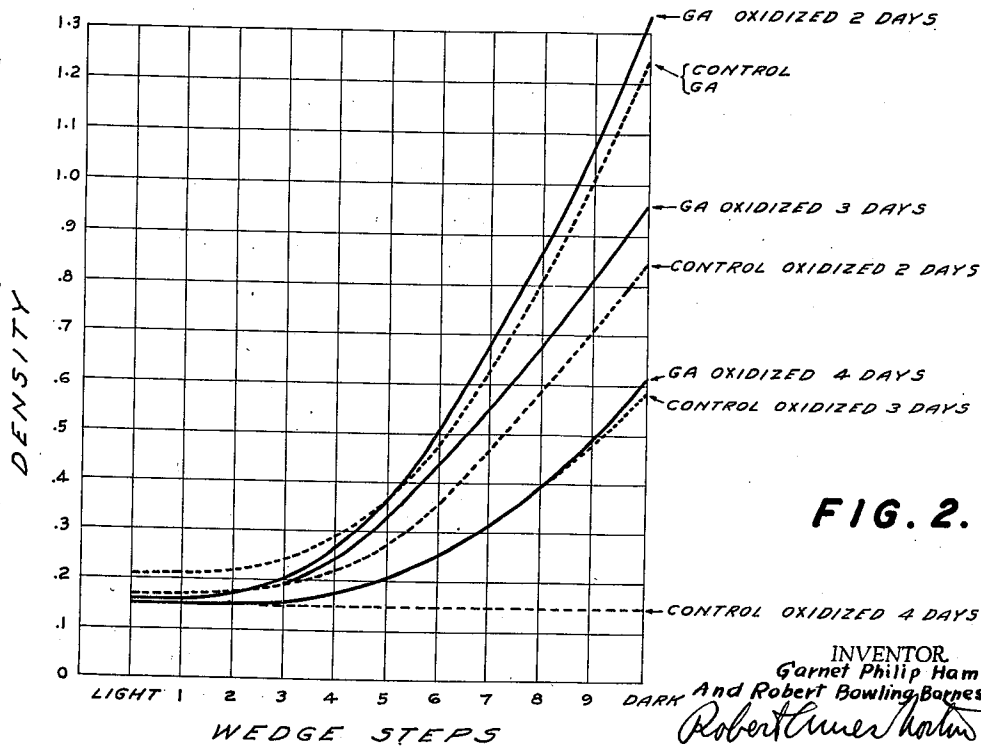


FIG. 2.

INVENTOR
Garnet Philip Ham
And Robert Bowling Barnes
Robert L. Ames
ATTORNEY.

Sept. 9, 1941.

G. P. HAM ET AL

2,255,731

PHOTOGRAPHIC DEVELOPER

Filed March 15, 1940

2 Sheets-Sheet 2

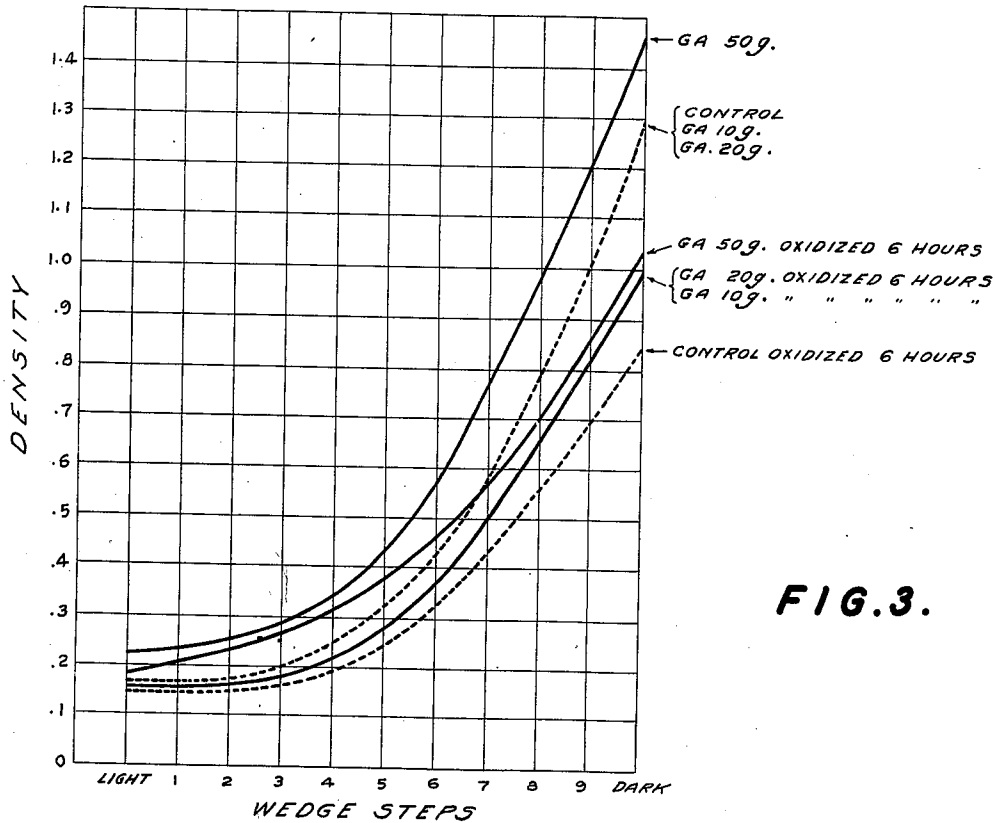


FIG. 3.

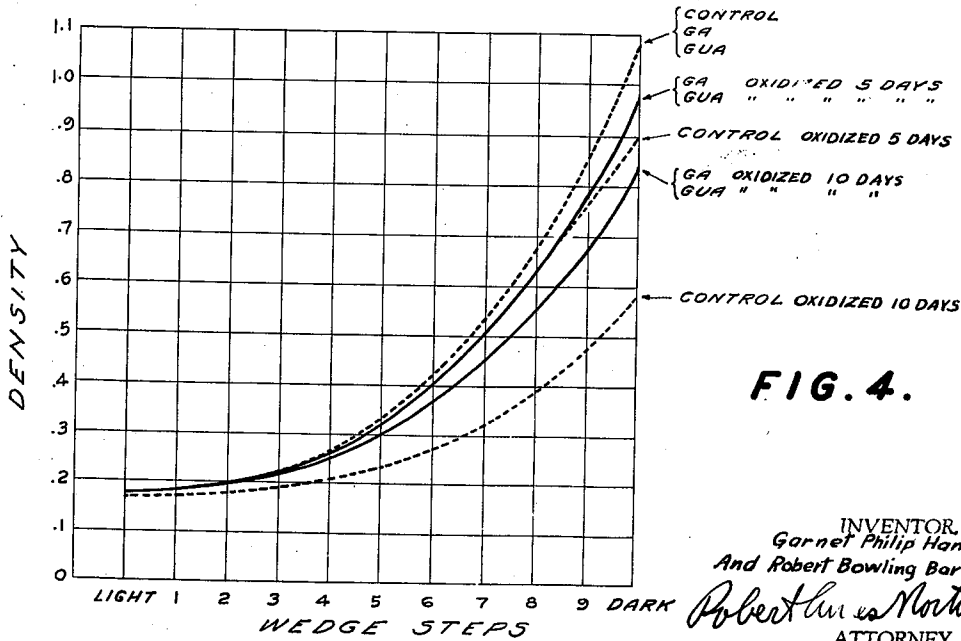


FIG. 4.

INVENTOR
Garner Philip Ham
And Robert Bowling Barnes
Robert A. Norton
ATTORNEY.

UNITED STATES PATENT OFFICE

2,255,731

PHOTOGRAPHIC DEVELOPER

Garnet Philip Ham, Riverside, and Robert Bowling Barnes, Stamford, Conn., assignors to American Cyanamid Company, New York, N. Y., a corporation of Maine

Application March 15, 1940, Serial No. 324,098

10 Claims. (Cl. 95—88)

This invention relates to improved silver halide photographic developers capable of withstanding aerial oxidation.

Photographic developers for silver halide material have a tendency to deteriorate if exposed to the air over long periods of time. The effect is even more pronounced in the strongly alkaline solutions of some high energy developers. In addition degradation compounds are formed in the solutions which materially retard the developing action, and if the developing solution is also exhausted through developing a large area of sensitive material, the effect of such silver complex sludges is greatly exaggerated.

In the past deterioration of alkaline developing solutions has been partly diminished by the inclusion of sodium or other soluble alkaline metal sulfites in the developing solution. It is thought that the sulfite acts as an oxidation inhibitor, being more readily oxidized than the developing agents themselves.

While sodium sulfite does produce a large measure of inhibition against aerial oxidation, there are certain classes of medium energy developing solutions and even those of low energy type which are by no means fully protected. Increasing the amount of the inhibitor in such solutions generally detracts from the efficiency of the developer due to the solvent action of the sulfite upon the latent image which obtains its best efficiency when the latent image is such that after development it possesses a density of approximately 0.8.

According to the present invention we have found that those developers which contain a soluble sulfite as oxidation inhibitors can be further fortified against aerial oxidation by the addition of an amidine salt of an aminobenzoic acid in the developing solution. Organic bases containing the



or amidine group such as benzamidine, acetamidine, guanidine, guanylurea, biguanide and their alkyl, hydroxyalkyl and aryl substitution products are sufficiently basic to enable them to form salts with such aminobenzoic acids as anthranilic acid, and the addition of such salts to photographic developing solutions constitutes the improvement of the present invention. While the invention broadly includes any amidine salts of any amino-benzoic acid, in a more specific aspect

we prefer to use salts of anthranilic acid and an amidine containing a guanyl radical such as guanidine anthranilate, biguanide anthranilate and guanylurea anthranilate.

The secondary inhibitors of the present invention may be added to any standard developing formula, the optimum amount varying with different developers. This is an advantage as the photographic technician may still employ his known solution and by adding the compounds of the present invention render his developing solutions more efficient for longer periods of time, thereby effecting great savings in cost. At the same time the quality of the development, that is, density, gradation, and contrast values are not diminished. In some instances the developers containing the inhibitors of the present invention, even after long exposure, have actually caused an increase in density over that originally obtained from the fresh developer. Furthermore, these secondary inhibitors do not cause any deleterious effect on the film material such as over-softening of the gelatin, nor are there any difficulties attendant with subsequent fixing or hardening such as reticulation, nor is there any noticeable change in the transmission or flexibility of the film support. Likewise, there is no effect on the grain size and distribution.

While it is not intended to limit our invention to any particular theory as to the mechanism by which this class of compounds contribute protection to the developer solutions against oxidation, we believe that they may either enter into a loose combination with the developing agents to form a new developer complex which has a decreasingly less affinity for atmospheric oxygen, or the new compounds themselves may act as anti-oxidants in the solution due to their low oxidation potential (approximately 0.4 V at 25°). Perhaps it is neither one nor the other, but a combination of these two factors, or some entirely different phenomenon that accounts for the great inhibiting effect of this class of compounds. Whatever the cause or theory of action, we have discovered that the use of such compounds in developing solutions enhances not only the keeping qualities, but as is pointed out above, in some cases densities are obtained exceeding those of the fresh developing solution. Thus poor quality developers, that is, those developers hitherto unfit for wide use due to their susceptibility to deterioration and other drawbacks such

as rapid exhaustion, can be made to serve efficiently over long periods of time.

The results obtainable by the present invention are illustrated in the drawings in which:

Fig. 1 is a series of curves obtained by a fine grain developing solution containing guanidine anthranilate, biguanide anthranilate and guanyl urea anthranilate, respectively;

Figs. 2 and 3 are similar sets of curves obtained by DK60 and DK50 developing solutions containing guanidine anthranilate; and

Fig. 4 is a series of curves obtained by a D19 developing solution containing guanidine anthranilate and guanyl urea anthranilate, respectively.

The invention will be further described in the following examples which show the use of secondary inhibitors of the present invention in various standard developing solutions. It is not intended, however, that these illustrations should in any way limit the scope of the present invention, for as stated above, any standard developing solution may be used. Furthermore, the amount of inhibitor compound to be used may vary within a wide range depending on the particular solution employed, the extent to which it is subject to oxidation, the alkalinity of the solution, and the length of exposure time to atmospheric oxidation.

In general we have found that amounts of from 1 to 5 grams per liter of solution are effective to give optimum results for most of the standard developers. Larger amounts do not show any increased effect, and in fact we have found that the addition of excessive quantities of the inhibitor has a retarding action on the developer. In some cases it may be found desirable to use a combination of inhibitors of the present invention to obtain some special result.

Example 1

Four developing solutions were prepared according to the following formula:

Water (85 to 90°)	ounces	26.00
Diotol F-R	grains	120
Monotol F-R	do	82
Sodium sulfite, anhydrous	ounces	2.75
Glycin	grains	22
Sodium phosphate, tribasic	do	45
Potassium bromide, U. S. P	do	3.50
Cold water added to	ounces	32

The components are mixed in the order given.

One solution was left as a control, and the other three were treated with 1 g. respectively of guanidine anthranilate (GA), biguanide anthranilate (BA) and guanylurea anthranilate (GUA) per 1000 ml. of developer solution. Portions of all four solutions at room temperature were then subjected to oxidation by bubbling air through at the rate of 1 bubble per second for a continuous 5-day period.

A photographic wedge with logarithmic steps representing a 50% increase in exposure from step to step, was contact printed onto a series of portions of 35 mm. supersensitive panchromatic film, using an extremely accurately controlled uniform exposure obtained by using as an exposing light a beam from a Leitz enlarger with the lens stopped down to its smallest opening.

A series of strips of film were then developed, one in each of the developing solutions both before and after oxidation, for a 16-minute period at 21° using stagnant development in each case. The densitometric values of the finished films

were measured and plotted as is shown in Fig. 1. A study of this graph indicates that all three solutions containing the secondary inhibitors showed a density greater than that of the control developer before oxidation. After being subjected to oxidation for five days the control did not show enough development to be measured, the developers containing guanylurea anthranilate and biguanide anthranilate were decreased in density somewhat but still showed good development, while the developer containing guanidine anthranilate actually showed better development after aerial oxidation than before, and much superior density than the fresh control.

Example 2

Two Eastman DK60 solutions were prepared according to the following formula:

Water	milliliters	500.00
Metol	grams	1.25
Sodium sulfite, des	do	15.00
Hydroquinone	do	1.25
Kodalk	do	10.00
Potassium bromide	do	0.25

One solution was left as a control, the other being treated with 5 g. of guanidine anthranilate per 1000 ml. of developer solution. Portions of both solutions were then subjected to the same oxidation as in Example 1. At the termination of a 2-day, 3-day and 4-day period photographic wedge strips, prepared as in Example 1, were developed in horizontal stagnant manner in each of the solutions for a 7-minute period at 18°. After fixing, the strips were measured on a densitometer, and the results plotted as is shown in Fig. 2.

The control solution after the 2-day oxidation had its density decreased from 1.25 to 0.85, whereas the solution containing the guanidine anthranilate showed a density of 1.33, greater than the density of the unoxidized control.

After three days the control density had dropped to about .58, whereas the density of the solution fortified with guanidine anthranilate was .95, and after four days of oxidation the control showed no development while the guanidine anthranilate still had a density of .6.

Example 3

Four Eastman DK50 solutions were prepared according to the following formula:

Water	milliliters	500.00
Metol	grams	1.25
Sodium sulfite, des	do	15.00
Hydroquinone	do	1.25
Kodalk	do	5.00
Potassium bromide	do	0.25

One solution was left as a control, the other three being treated with 10, 20 and 50 g. of guanidine anthranilate per 1000 ml. of developer. Portions of all four solutions were oxidized as described in Example 1 but the rate of air was increased to 5 bubbles per second, and oxidation continued for six hours.

Photographic wedge strips prepared as in Example 1 were developed stagnantly for a 7-minute period at 18° C., fixed, and the density measured and plotted as is shown in Fig. 3.

It is evident from a study of the graph that the solutions containing 10, 20 and 50 g. of the inhibitor per liter of developing solution after being subjected to oxidation still showed densities of approximately 1.0, but the control density had dropped from 1.3 to 0.85. However this test indi-

cates that increasing the amount of inhibitor does not materially increase the stability, for the densities of the developers containing 10 and 20 g. per liter of solution were the same, and the 50 g. only slightly higher.

Example 4

Three Eastman D19 solutions were prepared according to the following formula:

Water	-----	milliliters--	500.00	10
Metol	-----	grams--	1.10	
Sodium sulfite, des.	-----	do--	48.00	
Hydroquinone	-----	do--	4.40	
Sodium carbonate, des.	-----	do--	24.00	
Potassium bromide	-----	do--	2.50	15

One solution was left as a control, the other two being treated with 1 g. respectively of guanidine anthranilate and guanylurea anthranilate per 1000 ml. of developer. Portions of all three solutions were oxidized as in Example 1 continuously for 5 day and 10 day periods. Photographic wedge strips, prepared as in Example 1, were developed stagnantly for a 5-minute period at 18° C. and then fixed with a standard fixer. The strips were then measured on a densitometer and the curves obtained are shown in Fig. 4.

Example 5

Two 1 liter portions of the developer of Example 1 were prepared, one being used as a control and the other was treated with 1 gram of acetamidine anthranilate. Both portions of developer were divided into two parts, one part being blown with air for five days as described in Example 1. A wedge strip was printed on Eastman panatomic X35 mm. film as described in conjunction with the wedge strips on supersensitive film in Example 1. Four identically exposed strips were made, one strip being developed in the unoxidized control developer, another in the oxidized, and two more in the unoxidized and oxidized developer with the acetamidine anthranilate. The control developer after five days' oxidation showed no development at all, the result being the same as that obtained with a fast emulsion in Example 1. In the case of the oxidized developer to which the acetamidine anthranilate had been added blowing for five days had some effect but the developer still operated to

produce a satisfactory development. The inhibiting action of acetamidine anthranilate, while effective, is not quite as strong as that of guanidine anthranilate.

5 We claim:

1. A silver halide photographic developer containing at least one silver halide developing agent, a soluble sulfite and an effective amount of an amidine salt of an aminobenzoic acid.

10 2. A silver halide photographic developing solution containing at least one silver halide developing agent, a soluble sulfite and an effective amount of an amidine salt of an aminobenzoic acid, said amidine salt containing a guanyl radical.

15 3. A metol-hydroquinone photographic developing solution containing a soluble sulfite and an effective amount of an amidine salt of an aminobenzoic acid.

20 4. A metol-hydroquinone photographic developer containing a soluble sulfite and an effective amount of an amidine salt of an aminobenzoic acid, said amidine salt containing a guanyl radical.

25 5. A silver halide photographic developing solution containing at least one silver halide developing agent, a soluble sulfite and an effective amount of an amidine salt of anthranilic acid.

30 6. A silver halide photographic developing solution containing at least one silver halide developing agent, a soluble sulfite and an effective amount of an amidine salt of anthranilic acid, said amidine salt containing a guanyl radical.

35 7. A metol-hydroquinone photographic developing solution containing a soluble sulfite and an effective amount of an amidine salt of anthranilic acid, said amidine salt containing a guanyl radical.

40 8. A metol-hydroquinone photographic developing solution containing a soluble sulfite and guanidine anthranilate in effective amounts.

45 9. A metol-hydroquinone photographic developing solution containing a soluble sulfite and biguanide anthranilate in effective amounts.

10. A metol-hydroquinone photographic developing solution containing a soluble sulfite and guanyl urea anthranilate in effective amounts.

ROBERT BOWLING BARNES.
GARNET PHILIP HAM.