

July 9, 1974

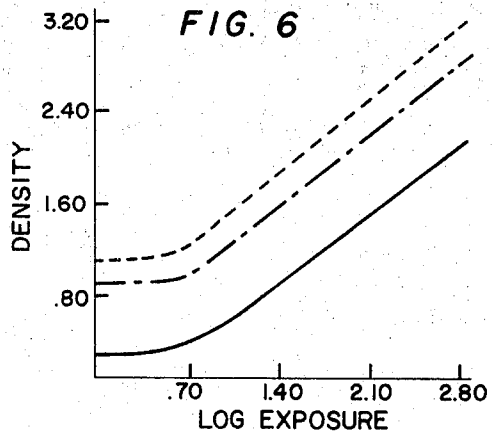
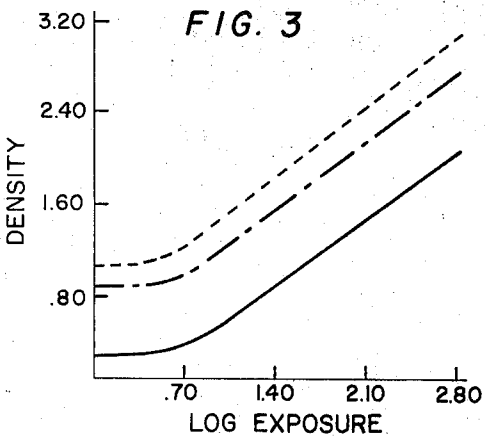
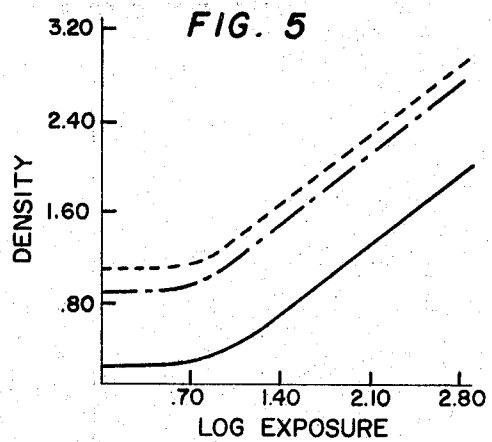
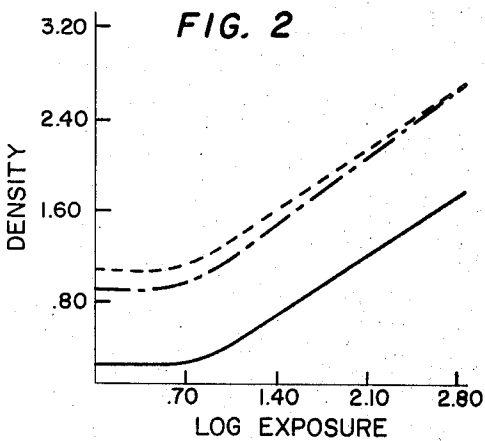
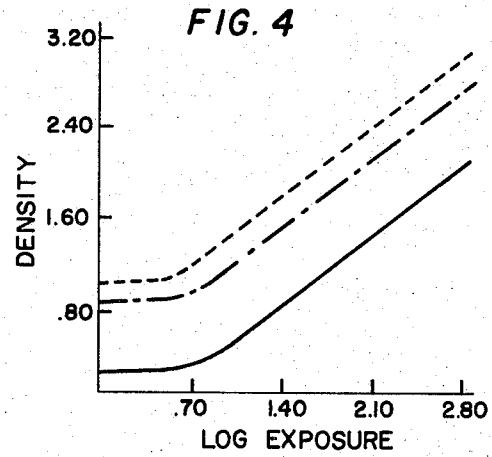
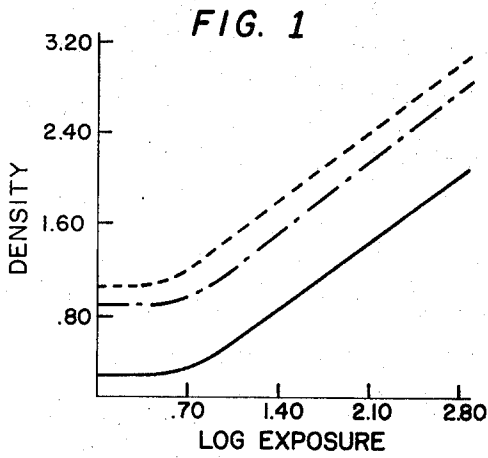
H. A. HODES

3,823,017

COLOR PHOTOGRAPHIC DEVELOPER COMPOSITIONS

Filed April 5, 1973

2 Sheets-Sheet 1



LEGEND:

- BLUE
- GREEN
- RED

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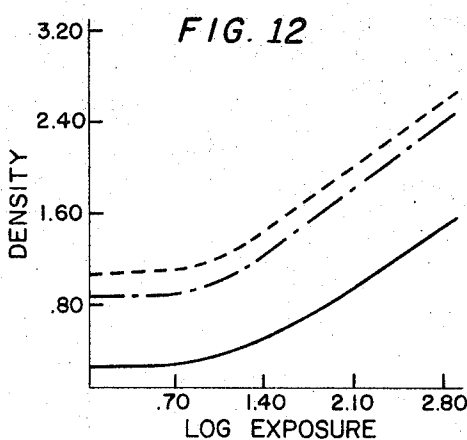
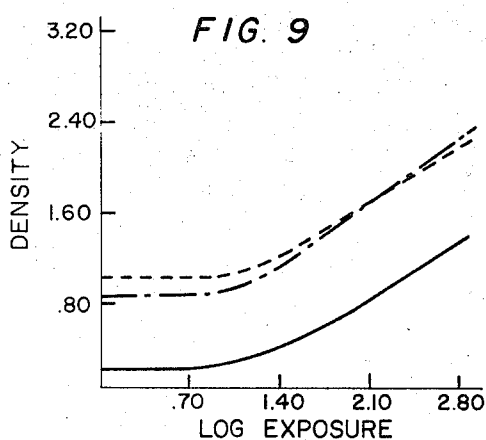
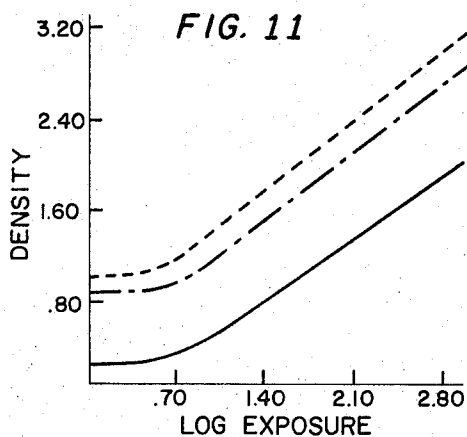
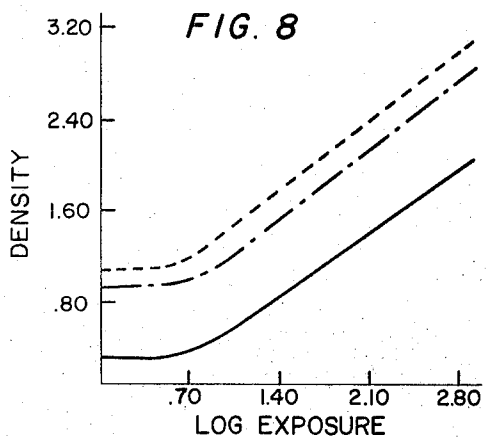
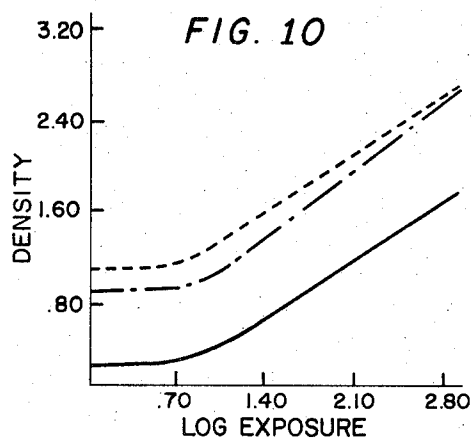
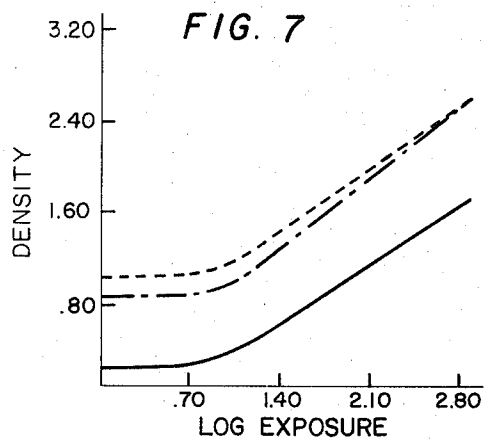
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COLOR PHOTOGRAPHIC DEVELOPER COMPOSITIONS

Filed April 5, 1973

2 Sheets-Sheet 2



LEGEND:

----- BLUE
- . - . - GREEN
————— RED

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3,823,017

COLOR PHOTOGRAPHIC DEVELOPER COMPOSITIONS

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U.S. Cl. 96-66.4

3 Claims

ABSTRACT OF THE DISCLOSURE

A color photographic developer composition of improved stability to aerial oxidation is obtained by including 2-anilinoethanol in the developer composition.

This invention relates in general to color photographic developer compositions and in particular, to a color photographic developer composition having improved stability to aerial oxidation.

BACKGROUND OF THE INVENTION

Exposed color film is usually developed in processing tanks containing the color photographic developer solution. During the processing steps, considerable aeration (oxidation) is produced by the passage of film through this developer solution, and by the exposure of the developer solution to atmospheric air. This type of aerial oxidation, if uncorrected by replenishing the developer with fresh solution, soon leads to serious loss in developer activity. Moreover, the problems of replenishing used color developer solutions is more complex than for conventional black and white processing, and are not easy to solve. That is, more complex chemical reactions occur during color development. Then too, higher pH levels are used in color developing compositions, and it is well known that these higher pH values render color developers more susceptible to aerial oxidation. Moreover, there are more complex sensitometric requirements in color photographic processing. Color photographic developer chemicals are also more expensive than those used in black and white processing.

SUMMARY OF THE INVENTION

The general object of this invention is to minimize or eliminate the above described difficulties with present color photographic developing compositions. A further object of this invention is to extend the useful life of color photographic developer compositions by inhibiting the aerial oxidation of these compositions during the processing stage. Another object of this invention is to preserve and lengthen the useful life of color photographic developing solutions in storage, until needed for actual developing and processing. Still another object of this invention is to provide an improved color developing composition which is substantially more stable to aerial oxidation than is obtained by present practice.

I have now found that the addition of 2-anilinoethanol as an antioxidant in an amount from about 0.1 to 0.15 percent by volume of the developer composition is a simple, inexpensive, and effective means of accomplishing the above enumerated objectives of this invention.

All color developing agents included in developer compositions in common use today are derivatives of paraphenylenediamine. Such color developing agents include N,N - diethyl paraphenylenediamine hydrochloride; hydroxyethylethylparaphenylenediamine sulphate; and diethylamino-orthotoluidine hydrochloride. An example of a color developing agent in widespread use is β -methanesulphonamidoethyl ethyl amino toluidine sesquisulphate known in the trade as simply CD3 or CD3 color developing agent. It is with the compounds of the above type gen-

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erally as substituted paraphenylenediamines, that the antioxidant properties of 2-anilinoethanol are most effective.

A typical color developing composition as known in the art would contain the following ingredients:

5 TYPICAL COLOR DEVELOPING COMPOSITION

CD3	-----grams	7.5
Na ₂ SO ₃	-----do	2.0
Benzyl alcohol	-----ml	5.0
NaOH	-----grams	15.0
Borax	-----do	60.0
KBr	-----do	1.5
Water to make 1 liter.		
pH is adjusted to 11.5.		

15 A conventional multicolor, multilayer color film as for example Kodak Ektacolor Type S containing incorporated color forming couplers is exposed and then agitated at 75 degrees F. for 5½ minutes in the above solution, and then transferred to a combined bleach-fixing bath that contains the following ingredients:

COMBINED BLEACH-FIXING BATH

		Grams
25 Ammonium thiosulfate	-----	100.0
Iron salt of ethylene diamine tetracetic acid	----	100.0
Sodium sulfite	-----	6.7
Water to make 1 liter.		
pH is adjusted to 5.8-6.0.		

30 The film strip is agitated in the above bleach-fixing bath for 3 minutes, then left in running water for about 2 minutes, then removed and left to dry. The preceding is an example of a typical color photographic processing system containing CD3 as the color developing agent.

BRIEF DESCRIPTION OF THE DRAWING

The effect of including 2-anilinoethanol in the typical color developing composition is illustrated by the accompanying drawing wherein:

40 FIG. 1 is a characteristic H and D curve obtained from a three color densitometer scan of the typical color developing composition and discussed in the specification in the preferred embodiment;

45 FIG. 4 is a characteristic H and D curve obtained from a three color densitometer scan of the typical color developing composition as in FIG. 1 but containing 0.15 volume percent of 2-anilinoethanol and discussed in the specification in the preferred embodiment;

50 FIG. 2 is a characteristic H and D curve obtained from a three color densitometer scan of the typical color developing composition after the composition has stood for 5 days unprotected by 2-anilinoethanol and discussed in the specification in the preferred embodiment;

55 FIG. 5 is a characteristic H and D curve obtained from a three color densitometer scan of the typical color developing composition after the composition has stood for 5 days protected by the inclusion of 0.15 volume percent of 2-anilinoethanol and discussed in the specification in the preferred embodiment;

60 FIG. 3 is a characteristic H and D curve obtained from a three color densitometer scan of the typical color developing composition and discussed in the specification in Example 2;

65 FIG. 6 is a characteristic H and D curve obtained from a three color densitometer scan of the typical color developing composition as in FIG. 3 but containing 0.15 volume percent of 2-anilinoethanol and discussed in the specification in Example 2;

70 FIG. 7 is a characteristic H and D curve obtained from a three color densitometer scan of the typical color developing composition unprotected by 2-anilinoethanol and

after processing 5 feet of pre-exposed film and discussed in the specification in Example 2;

FIG. 10 is a characteristic H and D curve obtained from a three color densitometer scan of the typical color developing composition protected by the inclusion of 0.15 volume percent of 2-anilinoethanol and after processing 5 feet of pre-exposed film and discussed in the specification in Example 2;

FIG. 8 is a characteristic H and D curve obtained from a three color densitometer scan of the typical color developing composition and discussed in the specification in Example 3;

FIG. 11 is a characteristic H and D curve obtained from a three color densitometer scan of the typical color developing composition as in FIG. 8 but containing 0.15 volume percent of 2-anilinoethanol and discussed in the specification in Example 3;

FIG. 9 is a characteristic H and D curve obtained from a three color densitometer scan of the typical color developing composition unprotected by 2-anilinoethanol and subjected to air oxidation test and discussed in the specification in Example 3; and

FIG. 12 is a characteristic H and D curve obtained from a three color densitometer scan of the typical color developing composition as in FIG. 9 but protected by 2-anilinoethanol and subjected to air oxidation test and discussed in the specification in Example 3.

DESCRIPTION OF THE DRAWING AND PREFERRED EMBODIMENT

Example 1

The anti-oxidant and protective properties of 2-anilinoethanol are evaluated in the following manner.

One liter of the typical color developing composition is prepared as per the formulation given. This formulation is then divided into two 500 ml. portions. One portion is labeled 1 and designated as the control. To the other 500 ml. portion is added 0.75 ml. or 0.15 percent by volume of 2-anilinoethanol. This portion is labeled 4. An exposed step wedge is then developed in portion labeled 1, and another in portion labeled 4. After completion of processing, the dried film strips are scanned by a recording densitometer which records the individual color film components—red, green, blue. The resultant characteristic H and D curves are shown respectively in FIG. 1 and FIG. 4 of the drawing.

Both portions are then placed in 500 ml. beakers, uncovered, and with the liquid levels marked. They are allowed to remain undisturbed for a period of five days. At the end of the five day period, the amount of liquid evaporated is replaced with water. Next film strips, exactly as before are developed in portion labeled 1 and portion labeled 4. Again, as before, the film strips are scanned by a recording densitometer which records the individual color film components—red, green, blue. The resulting characteristic H and D curves are shown respectively in FIG. 2 and FIG. 5 of the drawing. These represent the analogs of portion labeled 1 and portion labeled 4 after standing five days.

Examination of characteristic H and D curves resulting from the densitometer readings show that FIG. 1 or control, and FIG. 4 or control plus 0.75 ml. anti-oxidant are essentially superimposable—or to state it another way—the addition of the anti-oxidant does not affect the developer. This is important, since previous work in this field indicates that most anti-oxidants depress the sensitometric curves, that is, they lower developer activity.

Next, the characteristic H and D curves shown respectively in FIG. 2 and FIG. 5 of the drawing are examined. On superimposing one curve on another, the difference between the two samples become obvious. In FIG. 2 which is without the anti-oxidant, the blue and green lines have converged. A satisfactory color print can no longer be made from a negative processed in this solution. Again, as compared to the original solution, FIG. 1

or control, the entire set of curves is depressed, showing serious loss in developer activity. However, an examination of FIG. 5 which is protected by the anti-oxidant shows a marked improvement as compared to FIG. 2. The curves of FIG. 5 are still essentially parallel, indicating that a satisfactory print could still be made from a negative developed in this solution. Again, comparing FIG. 4 with the same sample as seen in FIG. 5, after five days, shows that the curves are depressed but not nearly so much as the unprotected solutions. This demonstrates the anti-oxidant and protective action of 2-anilinoethanol under static conditions.

Example 2

A more vigorous test of the anti-oxidant properties of 2-anilinoethanol is to compare the activity of a developer protected with 2-anilinoethanol to the same developer under conditions obtaining in actual practice—that is, to develop enough film in a given quantity of developer so as to practically exhaust the developer, and then compare results between developers protected with 2-anilinoethanol and unprotected developers. No previous work in the field has discussed this aspect of anti-oxidant effectiveness, although from the practical standpoint, anti-oxidant protection is more valuable during actual processing conditions than under static storage conditions. These tests are carried out as follows:

Just as in the previous illustration, one liter of typical color developing composition is prepared and divided into two 500 ml. portions. One portion labeled 3 is kept as a control; the other portion labeled 6 has 0.75 ml. of 2-anilinoethanol added to it. Next film strips, exactly as in the first illustration, are processed, and the film strips then scanned on a recording densitometer which plots individual curves of the three primary colors—red, green, blue. These curves are shown respectively in FIG. 3 and FIG. 6. Then, five feet of completely exposed film of the same type and dimensions as those used in making the test film strips are agitated in the usual manner for a 5½ minute period in the developer. Next, the degree of developer exhaustion is determined by running another film strip (exposed to a step wedge, as before) through the developer and bleach fix. FIG. 7 and FIG. 10 respectively of the drawing represent characteristic H and D curves obtained from the resultant densitometer scans. Although not so dramatic as in the static storage test, these results show a lower maximum density and more convergence—that is, less parallelism—of the unprotected developer or FIG. 7 of the drawing for the green and blue lines. This again would produce a less satisfactory print than in the protected developer.

Example 3

The anti-oxidant and protective properties of 2-anilinoethanol under conditions of accelerated aging is evaluated as follows.

Just as in the previous examples, a liter of typical color developing composition is prepared and divided into two 500 ml. portions. One portion labeled 8 is kept as the control, the other portion labeled 11 has 0.75 ml. of 2-anilinoethanol added. Sensitometric strips are developed in these two developers in the usual manner, and the processed strips are then scanned on an automatic recording densitometer which plots individually each primary color, red, green, and blue. FIG. 8 or the control, and FIG. 11 or the control plus 0.75 ml. 2-anilinoethanol, are the resultant characteristic H and D curves. Next, each of the above solutions is placed in a 500 ml. Erlenmeyer flask which is connected to an aspirator pump. Room air is then bubbled through these solutions at a rate of about 2 liters a minute for a total time of seven hours. Next, sensitometric strips are processed in the two solutions, exactly as before, and the strips scanned. The resultant curves are shown respectively in FIG. 9 or control plus 7 hours air and FIG. 12 or control plus 0.75 ml. 2-

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anilinoethanol plus 7 hours air. The differences between the two sets of characteristic curves are striking and illustrate the protective action furnished by the 2-anilinoethanol under drastic conditions of air oxidation. When referring to FIG. 9 and comparing it to FIG. 8, one sees that the entire set of curves is very much depressed from the control, indicating a great loss in developer activity. Moreover, the blue and green lines are no longer parallel, but converge. This indicates that a color print made from a negative processed in this solution would no longer have the correct color balance compared to one made from the original control or FIG. 8. Now, referring to FIG. 9 and comparing it to FIG. 12, the situation is quite different. The curves of FIG. 12 are depressed but nowhere to the extent of the unprotected solution. The curves are still parallel, showing that even after this drastic treatment, the developer protected by 2-anilinoethanol is still usable, and a negative processed in this solution would still make a satisfactory color print.

While there has been described what is at present considered to be the preferred embodiment of this invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the invention.

What is claimed is:

1. In a color photographic developer composition containing a substituted paraphenylenediamine as the color-developing agent, the improvement of adding about 0.1

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to 0.15 percent by volume of 2-anilinoethanol to the developer composition.

2. An improved color photographic developer composition according to Claim 1 in which β -methanesulphonamidoethyl ethyl amino toluidine sesquisulfate hydrate is the color developing agent.

3. An improved color photographic developer composition according to Claim 1 consisting of the following ingredients:

10	β -methanesulphonamidoethyl ethyl amino toluidine sesquisulfate hydrate	grams	7.5
	Na_2SO_3	do	2.0
	Benzyl alcohol	milliliters	5.0
	NaOH	grams	15.0
15	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	do	60.0
	KBr	do	1.5
	2-anilinoethanol	milliliters	0.75
	Water to make 1 liter.		
	pH is adjusted to 11.5.		

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