Aug. 27, 1974 C. O. EDENS **3,832,179**

INHIBITION OF FOG IN PHOTOGRAPHIC COLOR DEVELOPMENT

Filed Jan. 24, 1973 3 Sheets-Sheet 1

FIG. 1

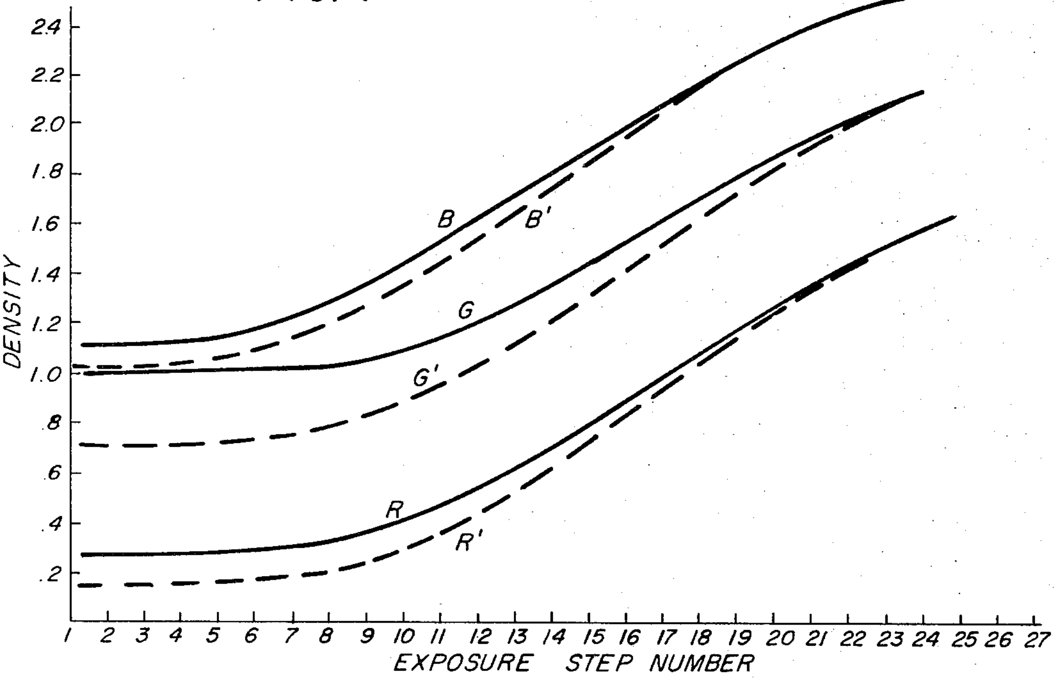


FIG. 2

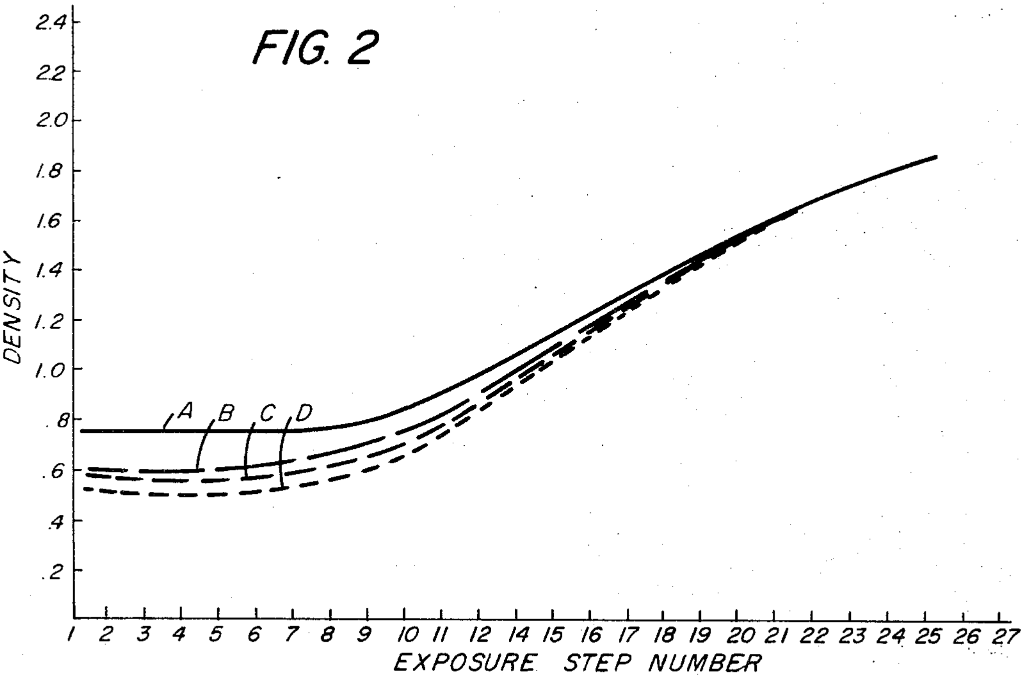
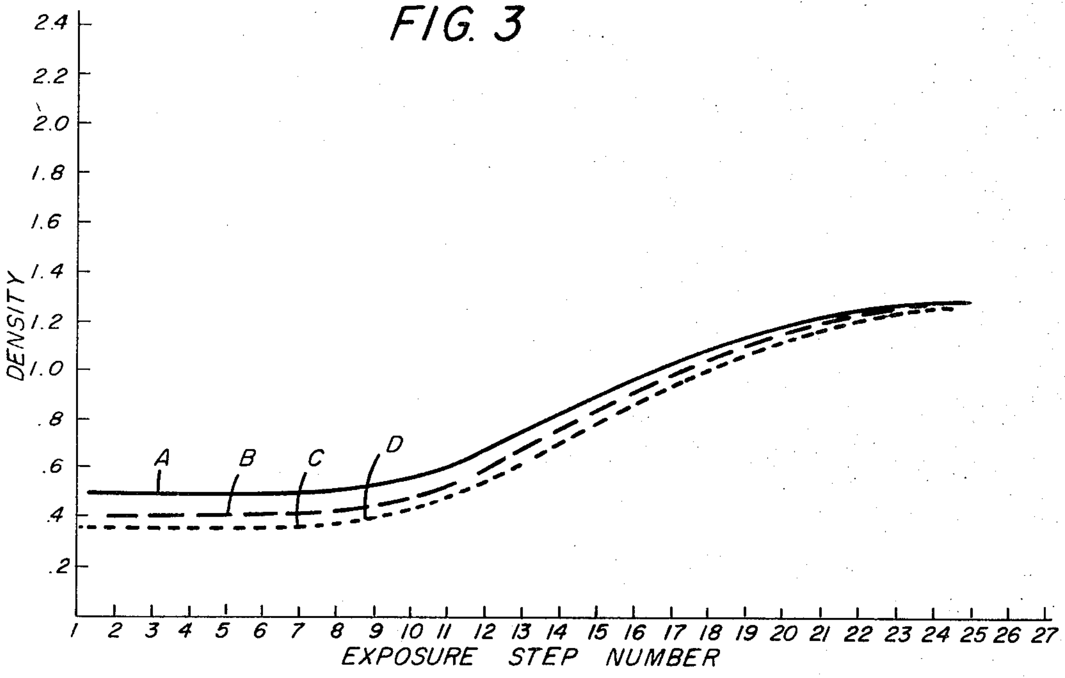


FIG. 3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2.2
2.0
1.8
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1.4
1.2
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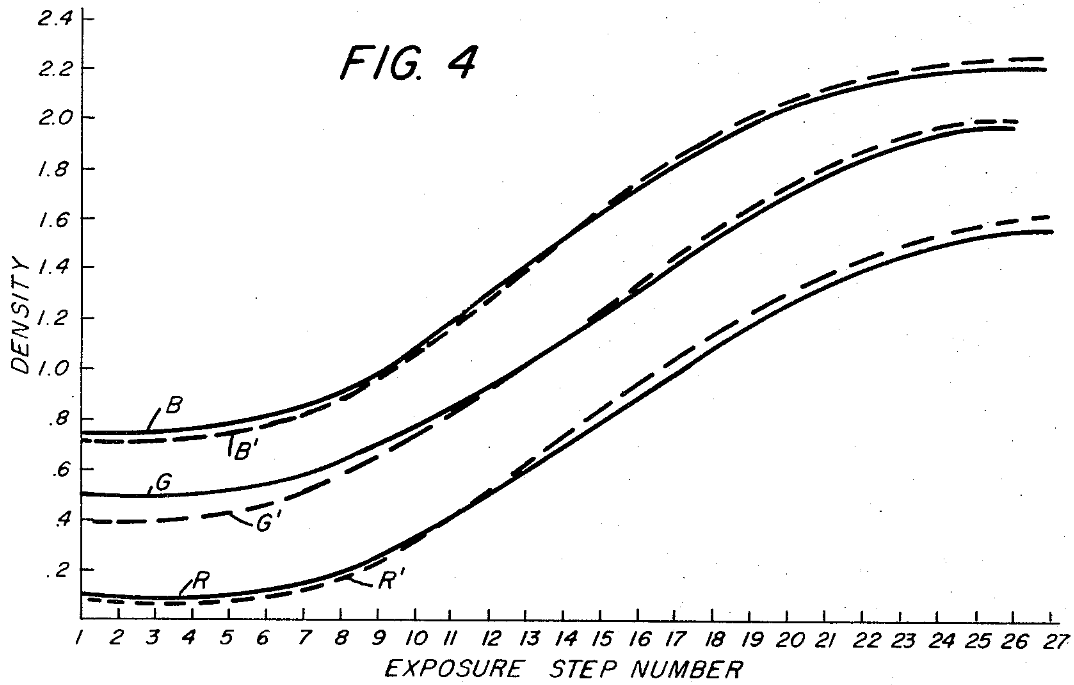
.8
.6
.4
.2
DENSITY
A
B
C
D
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27
EXPOSURE STEP NUMBER

FIG. 4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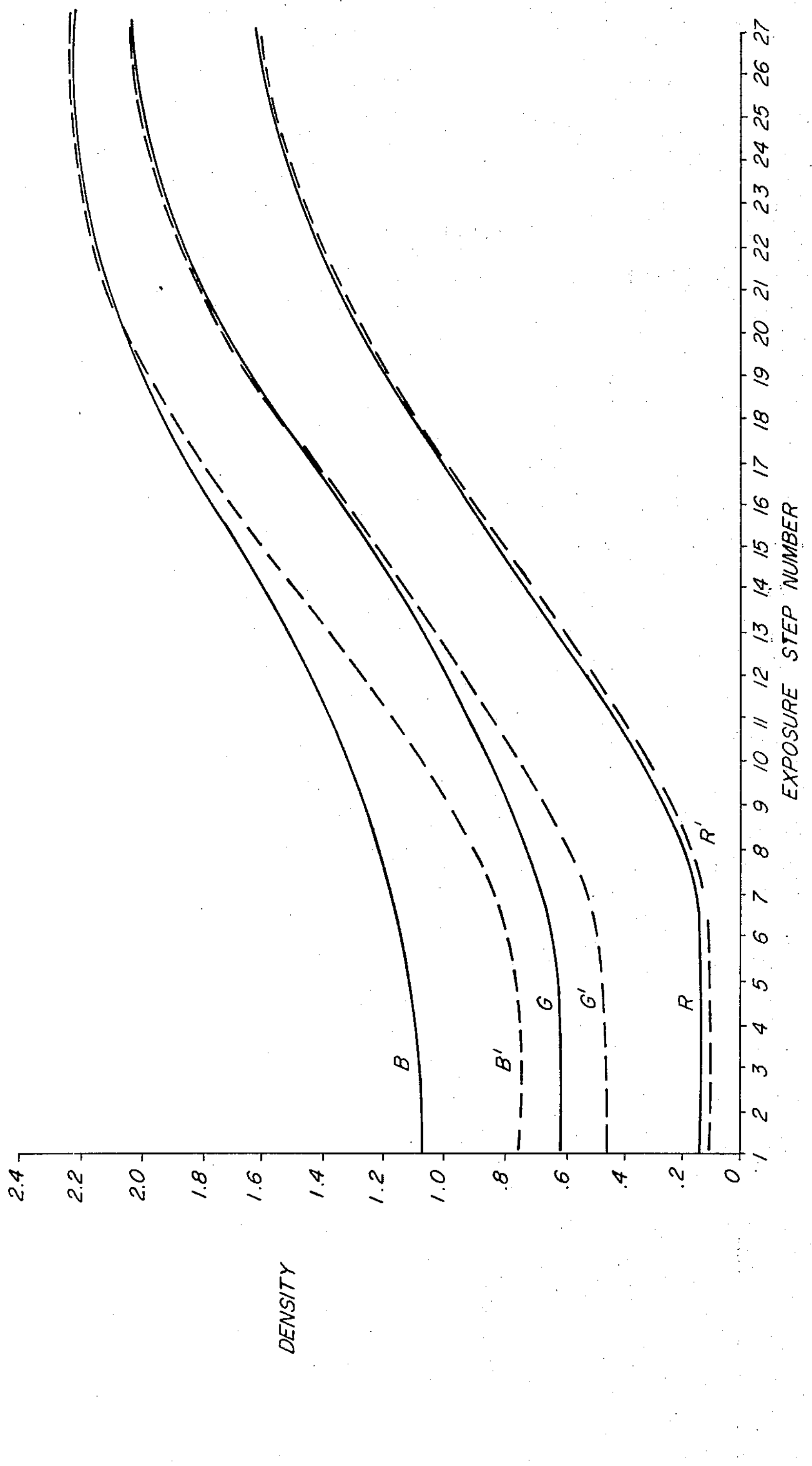
DENSITY
B
B'
G
G'
R
R'
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27
EXPOSURE STEP NUMBER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1.6
1.8
2.0
2.2
2.4
EXPOSURE STEP NUMBER
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
B
B'
G
G'
R
R'

FIG. 5

United States Patent Office

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INHIBITION OF FOG IN PHOTOGRAPHIC COLOR DEVELOPMENT

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ABSTRACT OF THE DISCLOSURE

In processing multilayer color photographic elements the formation of fog is suppressed by carrying out the development of the element in a color developer solution containing a nitro-substituted benzoic acid, such as 3,5 - dinitrobenzoic acid. The nitro - substituted benzoic acid functions effectively to suppress magenta and yellow fog and, to a lesser extent, to suppress cyan fog.

This invention relates in general to color photography and in particular to methods and compositions for color development. More specifically, this invention relates to the suppression of fog formation during development of multi-layer color photographic elements.

The system of three-color photography suggested by Fischer in U.S. Pat. 1,055,155 issued Mar. 4, 1913 is the basis of several color photographic processes and products which have come into widespread use. In this system, color development of exposed silver halide emulsion layers is accomplished by means of a primary aromatic amino silver halide developing agent in the presence of color-forming coupler compounds. During the color development step the coupler compounds react with the oxidation product of the developing agent to form dye images in situ with the developed silver image. The silver image and residual silver halide are then removed from the photographic element by bleaching and fixing according to well known methods. It is common practice in systems of this type to provide a three-layer photographic element in which, for example, the upper emulsion layer is selectively sensitized to blue light, the next lower layer to green light and the lower-most layer to red light. Photographic elements of this description may be designed to produce a color negative for use in making positive color prints or transparencies or may be designed to yield a positive transparency directly by a reversal process.

In one form of a reversal process the photographic element is first developed with a black and white developing agent to form a negative silver image in each of the exposed emulsion layers. The colors of the dye images are determined by selectively and individually fogging the three emulsion layers and then subjecting each layer to a separate color development operation with a developer solution containing an appropriate color-forming coupler, i.e. a coupler adapted to form a dye of a color complementary to the predominant color sensitivity of the particular emulsion layer being treated. For example, the red sensitive layer of a color photographic element is uniformly fogged, after black-and-white development, and then subjected to color development with a color developer containing a coupler compound capable of forming a cyan dye with the oxidation product of the color developing agent formed during development. In a similar way the blue sensitive emulsion layer is fogged and subjected to color development with a color developer containing a yellow dye-forming coupler and the green sensitive layer is uniformly fogged and subjected to color development with a developer containing a magenta dye-forming coupler. The silver images and any residual silver halide in the several emulsion layers are then removed by bleaching and fixing to produce a natural color positive transparency comprising the three superposed dye images.

Typical processes of this type are disclosed in Fischer U.S. Pat. 1,102,028 issued June 30, 1914, Mannes and Godowsky U.S. Pat. 2,039,730 issued May 5, 1936, Mannes and Godowsky U.S. Pat. 2,108,602 issue Feb. 16, 1938, and Mannes and Godowsky U.S. Pat. 2,252,718 issued Aug. 19, 1941.

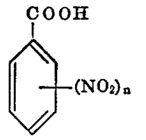
Another system of color photography employs the color development process to obtain a color negative. In this system a different color-forming coupler compound is incorporated in each of the emulsion layers of the color photographic element as originally suggested by Fischer in U.S. Pat. 1,055,155. Inasmuch as each of the three differently sensitized emulsion layers contains its own coupler adapted to form a dye complementary in color to the sensitivity of the emulsion layer, only one color development operation is needed to form the dye images in all of the emulsion layers simultaneously. Typical processes of this type are disclosed in Mannes and Godowsky U.S. Pats. 2,304,939 and 2,304,940 issued Dec. 15, 1942. These patents also disclose specific couplers adapted to be dispersed in the emulsion layers. Other couplers useful in methods of this type are disclosed in Jelley et al. U.S. Pat. 2,322,027 issued June 15, 1943, Fierke et al. U.S. Pat. 2.801,171 issued July 30, 1957 and in Porter et al. U.S. Pat. 2,369,489 issued Feb. 13, 1945 as well as in other patents.

Specific couplers useful in photographic color processes in which the coupler is present in the developer rather than in the emulsion layer are disclosed in such representative references as Mannes and Godowsky U.S. Pat. 2,039,730 issued May 5, 1936, Mannes and Godowsky U.S. Pat. 2,108,602 issued Feb. 15, 1938 and Mannes and Godowsky U.S. Pat. 2,115,394 issued Apr. 26, 1938.

Although color photographic processes and products employing color development have proven successful, the art has sought methods of increasing the efficiency of the color development operation and the photographic quality of the dye images obtained. To this end, numerous addenda have been added to color developing solutions for the purpose of modifying the development and storage characteristics of such solutions. In particular, the provision of effective means for suppressing fog formation on color development has long been sought and a wide variety of compounds have been proposed heretofore for this use. It is toward the objective of suppressing fog formation upon color development of a multilayer photographic element by the use of a novel antifoggant that the present invention is directed.

It has now been discovered that nitro-substituted benzoicacids are effective as antifoggants for use in suppressing fog formation upon color development. They have been found to be especially effective in reducing magenta fog and yellow fog and, to a lesser extent, cyan fog. The nitro-substituted benzoic acids can be utilized as antifoggants with photographic elements which are designed to be processed in color developers containing couplers or with photographic elements which contain the coupler in the silver halide emulsion layers or in layers contiguous thereto. In either case, they are incorporated in a fog-inhibiting amount in the color developer solution in order to provide the desired suppression of fog formation.

The nitro-substituted benzoic acid antifoggants of this invention can contain one or more nitro group substituents. They can be represented by the formula:



wherein *n* is an integer having a value of at least one and preferably a value of two.

Illustrative examples of such nitro-substituted benzoic acids are

2,4-dinitrobenzoic acid
3,4-dinitrobenzoic acid
2,5-dinitrobenzoic acid
3,5-dinitrobenzoic acid
o-nitrobenzoic acid
m-nitrobenzoic acid
p-nitrobenzoic acid
2,4,6-trinitrobenzoic acid,

and the like.

The nitro-substituted benzoic acids can be used in any amount which is sufficient to inhibit fog formation. They are preferably employed in an amount of from about 0.01 to about 10 grams per liter of color developing solution and more preferably in an amount of from about 0.1 to about 1 gram per liter of color developing solution.

Typically, the developing agent included in the color developing solution is a primary aromatic amino color developing agent such as a p-phenylenediamine. Developing agents of this type are usually used in the salt form, such as the hydrochloride or sulfate, as the salt form is more stable than the free amine, and are generally employed in concentrations of from about 0.1 to about 10 grams per liter of solution and more preferably from about 0.5 to about 5 grams per liter of solution. These developing agents include p-phenylenediamine and N,N-dialkyl - p - phenylenediamines wherein the alkyl groups or the aromatic nucleus may be substituted, for example:

N,N-diethyl-p-phenylenediamine monohydrochloride,
2-amino-5-diethylaminotoluene monohydrochloride,
4-amino-N-ethyl-N-[β-methanesulfonamidoethyl]-m-toluidine sesquisulfate monohydrate,
4-amino-3-methyl-N-ethyl-N-[β-hydroxyethyl]-aniline sulfate,
4-amino-3(β-methylsulfonamidoethyl)-N,N-diethylaniline hydrochloride,
4-amino-N,N-diethyl-3-(N′-methyl-β-methylsulfonamido)-aniline hydrochloride

and similar color developing agents disclosed in U.S. Pat. Nos. 2,552,241 and 2,566,271. Other useful p-phenylenediamine developing agents are disclosed in J.A.C.S. 73, 3100–3125, (1951). Especially effective p-phenylenediamines are those containing at least one alkylsulfonamidoalkyl substituent attached to the aromatic nucleus or to an amino nitrogen. In some instances, a "competing" developing agent will be included in the developer solution in addition to the aforesaid primary aromatic amino color developing agent.

Developing compositions containing nitro-substituted benzoic acids as antifoggants, in accordance with the present invention, can also contain any of the various components that are ordinarily incorporated in color developing solutions, for example, materials such as alkalies, alkali metal sulfites, alkali metal bisulfites, alkali metal thiocyanates, alkali metal bromides, alkali metal iodides, thickening agents, water softening agents, and so forth. The pH of the developing solution is ordinarily above 7 and most typically about 10 to about 13.

Development of photographic elements in a color developer solution containing a fog-inhibiting amount of a nitro-substituted benzoic acid, in accordance with the present invention, can be advantageously employed in the processing of photographic elements designed for reversal color processing, or in the processing of negative color elements or color print materials. The photosensitive layers present in the photographic elements processed according to the method of this invention can contain any of the conventional silver halides as the photosensitive material, for example, silver chloride, silver bromide, silver bromoiodide, silver chlorobromide, silver chloroiodide, silver chlorobromoiodide, and mixtures thereof. The emulsion layers can contain conventional addenda and be coated on any of the photographic supports, such as, for example, cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polycarbonate film, polystyrene film, polyethylene terephthalate film, paper, polymer-coated paper, and the like.

The antifoggants of this invention are especially useful because they can be employed over a wide range of concentrations with effective results and thus the process in which they are employed need not be precisely regulated with respect to concentration of the antifoggant. Unlike many prior art antifoggants which adversely affect speed they provide effective antifoggant activity without such undesirable results. They reduce fog inherent to the silver halide emulsion as well as preventing or counteracting fog caused by contaminants in the developer solution.

The invention is further illustrated by the following examples of its practice.

EXAMPLE 1

A multilayer color negative photographic film of composition and structure essentially as described in Example 5 of United States Pat. 2,860,974 and Example 2 of United States Pat. 3,034,892 was exposed through a multicolor 0.15 log E graduated-density step tablet and then processed at 100° F. in the following sequence:

	min.
Color developer	3½
Bleach-fix	3
Wash	2
Stabilizer	10 seconds

One portion of the film, designated test sample A, was processed in the above sequence using a color developer, bleach-fix and stabilizer of the following compositions:

Color Developer

Water	ml.	800
Benzyl alcohol	ml.	5
Sodium polyphosphate	gm.	2.5
Sodium sulfite	gm.	1.85
Sodium bromide	gm.	1.4
Potassium iodide	mg.	0.5
Sodium hydroxide	gm.	12.5
Sodium tetraborate	gm.	44.9
4-Amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)ethylaniline sulfate hydrate	gm.	5.0

Water to 1 liter (pH 10.7)

Bleach-fix

Water	ml.	800
Ammonium thiocyanate	gm.	200
Ferris salt of ethylenediaminetetra-acetic acid	gm.	200
Tetra sodium salt of ethylenediaminetetraacetic acid	gm.	5

Water to 1 liter

Stabilizer

Water	ml.	800
Sodium polyphosphate	gm.	0.2
Formalin	ml.	1.0

Water to 1 liter

A second portion of the film, designated test sample A′, was processed under the same conditions and using the same processing solutions except that the color developer also contained 0.5 grams of 3,5-dinitrobenzoic acid per liter of solution.

Processed test samples A and A′ were sensitometrically evaluated by recording the characteristic curves of the developed yellow, magenta and cyan dye images. The characteristic curves for test sample A, identified by the letters B, G, and R for the yellow, magenta and cyan dye images respectively, are shown in Figure 1 which is a plot of density versus exposure step number. The exposure step numbers 1 to 27 represent the series of steps of the 0.15 log E graduated-density step tablet through which the test samples were exposed prior to processing, step No. 1

representing the highest, and step No. 27 the lowest density levels in the step tablet. The characteristic curves for test sample A′ are also shown in FIG. 1 and are identified by the letters B′, G′ and R′ for the yellow, magenta and cyan dye images respectively.

The results shown in Figure 1 demonstrate the effectiveness of the 3,5-dinitrobenzoic acid in suppressing fog in all three color images. Similar results are obtained by replacing the 3,5-dinitrobenzoic acid with other nitro-substituted benzoic acids such as

2,4-dinitrobenzoic acid,
2,5-dinitrobenzoic acid,
3,4-dinitrobenzoic acid,
o-nitrobenzoic acid,
m-nitrobenzoic acid,
p-nitrobenzoic acid, and
2,4,6-trinitrobenzoic acid.

EXAMPLE 2

A multilayer color negative photographic film similar to that described in Example 1 except that the emulsion layers are of lesser thickness was processed in the same manner as described in Example 1 with the color developer solution containing varying amounts of 3,5-dinitrobenzoic acid. The characteristic curve of the yellow developed dye image is shown in FIG. 2 which is a plot of density versus exposure step number similar to that of FIG. 1. In FIG. 2, the curves designated by the letters A, B, C and D represent, respectively, zero, 0.2, 0.5 and 1.0 grams of 3,5-dinitrobenzoic acid per liter of color developing solution. The characteristic curve of the magenta dye image is shown in FIG. 3 in which the curves designated by the letters A, B, C, and D also represent, respectively, zero, 0.2, 0.5 and 1.0 grams of 3,5-dinitrobenzoic acid per liter of color developing solution. As shown by the results in FIGS. 2 and 3 the extent to which fog is suppressed increases with increasing concentration of 3,5-dinitrobenzoic acid.

EXAMPLE 3

A two-week keeping test was carried out in which a multilayer color negative photographic film similar to that described in Example 1 was processed in the same manner as that described in Example 1 with 3,5-dinitrobenzoic acid in the color developer at a concentration of 0.5 grams per liter. In carrying out this test, the film was processed in fresh developer solution and in developer solution that had been kept for 14 days (referred to herein as aged developer). For control purposes, a test was also carried out using fresh developer that did not contain 3,5-dinitrobenzoic acid. The D_{min} values that were obtained for red density (cyan dye image), green density (magenta dye image) and blue density (yellow dye image) are as follows:

	$D_{min.}$ of—		
Developer	Red	Green	Blue
Control	0.18	0.82	0.82
Fresh developer	0.16	0.52	0.60
Aged developer	0.16	0.50	0.62

These results show that fog was reduced on the fresh test and the 14-day test to essentially the same degree.

EXAMPLE 4

A multilayer color negative photographic motion picture film having a structure as described in the article "Color Negative and Color Positive Film for Motion Picture Use," W. T. Hanson, Jr., Journal of the Society of Motion Picture and Television Engineers, Vol. 58, page 223, Mar. 1952, was exposed through the step tablet described in Example 1 and then processed in the following sequence:

	Temperature, ° F.	Time	
		Minutes	Seconds
Prebath	106		15
Wash	106	3	
Color developer	106	3	
Stop	72		30
Wash	72	3	
Bleach	72	4	
Wash	72	3	
Fix	72	1	
Wash	72	3	
Stabilizer	72		15

In this process, the prebath was a carbonate solution designed for the removal of the antihalation "rem jet" backing from the film; the color developer solution was essentially the same as that described in Example 1 except that it contained no benzyl alcohol and had a pH of 10.2; the stop bath was a 3% solution of acetic acid; the bleach was a conventional ferric ethylenediaminetetraacetic acid bleach bath; the fix was a conventional thiosulfate fixing solution; and the stabilizer was the same as that described in Example 1.

Characteristic curves for the developed yellow, magenta and cyan dye images were recorded for a film sample processed in color developer that contained no 3,5-dinitrobenzoic acid and for a film sample processed in color developer that contained 0.2 grams of 3,5-dinitrobenzoic acid per liter of solution. These curves are shown in FIG. 4 with the curves identified by the letters B, G and R representing the yellow, magenta and cyan dye images respectively for processing with no 3,5-dinitrobenzoic acid in the developer solution and the curves identified by the letters B′, G′ and R′ representing the yellow, magenta and cyan dye images respectively for processing with 0.2 grams of 3,5-dinitrobenzoic acid per liter of developer solution. The results indicate that under the conditions of this test, the minimum densities of the yellow and cyan dye images are slightly reduced by the addition of 3,5-dinitrobenzoic acid while the density of the magenta dye image is substantially decreased. Thus, under these conditions, the 3,5-dinitrobenzoic acid is most effective in suppressing magenta fog.

EXAMPLE 5

The photographic film described in Example 4 was processed under the same conditions as described in Example 4 except that the color developing solution had been stored for five days at room temperature. The characteristic curves for this test are shown in FIG. 5 with curves B, G and R representing the yellow, magenta and cyan dye images for processing with color developer that contained no 3,5-dinitrobenzoic acid and had been stored five days and curves B′, G′ and R′ representing the yellow, magenta and cyan dye images for processing with color developer that contained 0.2 grams per liter of 3,5-dinitrobenzoic acid and had been stored five days. The results shown in FIG. 5 illustrate the effectiveness of the antifoggants of this invention in stabilizing a color developing solution during storage.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A method of suppressing the formation of fog in the color development of a silver halide multilayer photographic element which comprises color developing said element with a color developer solution containing a primary aromatic amino color developing agent and a fog-inhibiting amount of a nitro-substituted benzoic acid.

2. A method as claimed in claim 1 wherein the amount of said nitro-substituted benzoic acid in said color developing solution is from about 0.01 to about 10 grams per liter of solution.

3. A method as claimed in claim **1** wherein the amount of said nitro-substituted benzoic acid in said color developing solution is from about 0.1 to about 1 gram per liter of solution.

4. A method as claimed in claim **1** wherein said nitro-substituted benzoic acid is 3,5-dinitrobenzoic acid.

5. An aqueous alkaline photographic developing solution comprising a primary aromatic amino color developing agent and a fog-inhibiting amount of a nitro-substituted benzoic acid.

6. An aqueous alkaline photographic developing solution comprising a primary aromatic amino color developing agent and a fog-inhibiting amount of 3,5-dinitrobenzoic acid.

7. A developing solution as claimed in claim **5** wherein said color developing agent is a p-phenylenediamine color developing agent.

8. A developing solution as claimed in claim **5** wherein said color developing agent is 4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)ethylaniline.

9. A developing solution as claimed in claim **5** wherein the amount of said nitro-substituted benzoic acid in said solution is from about 0.01 to about 10 grams per liter of solution.

10. A developing solution as claimed in claim **5** wherein the amount of said nitro-substituted benzoic acid in said solution is from about 0.1 to about 1 gram per liter of solution.

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U.S. Cl. X.R.

96—22, 55, 66.5