

UNITED STATES PATENT OFFICE

2,490,758

FUCHSONE DYES IN A DIRECT POSITIVE PHOTOGRAPHIC PROCESS

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No Drawing. Application August 28, 1948,
Serial No. 46,714

6 Claims. (Cl. 95—88)

This invention relates to photography and particularly to a method of making direct positive photographs.

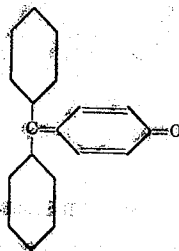
Direct positive effects may be produced by solarizing the developable latent image by over-exposure, by using a second exposure to obtain the Sabbatier or the Clayden effect or by redeveloping a developed negative image. Solarizable sensitized products require very intense exposures to obtain the desired direct positive photograph. The use of a second exposure has obvious disadvantages from the point of view of practical technique. Redevelopment adds at least two operations to the usual and normal developing procedure.

Fallesen U. S. application Ser. No. 780,405, filed October 17, 1947, describes forming a direct positive image in a suitable silver halide emulsion by exposing the emulsion in the usual way and developing it in a developer which is capable of giving aerial fog. The emulsion is preferably of the internal latent image type such as described in Davey and Knott U. S. application Serial No. 790,232, filed December 6, 1947, now abandoned.

For practical use in the documentary photographic copy field, a direct positive print process should possess certain features. The exposure required should be of the same order as that required for ordinary contact silver halide paper. With a minimum of processing steps, it should yield a positive image having clean whites and a reflection maximum density on non-baryta-coated stock of from 1.1 to 1.3 and it should possess adequate contrast or gamma and sufficiently short toe in the characteristic curve to render line copy in a crisp, clean manner. In addition, for machine processing, it is desirable to have the developing times for such material as short as can reasonably be controlled, preferably less than 60 seconds.

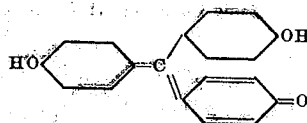
We have found that the rate and evenness of development in the high-density areas may be improved and in most cases, the minimum density may be lowered by processing a direct positive material of the type disclosed in Fallesen U. S. application, Serial No. 780,405 in formaldehyde-bisulfite-hydroquinone-developers of the type disclosed in Stauffer U. S. application 780,569, filed October 17, 1947, and also containing certain triphenyl methane dyes. The use of a triphenyl methane dye constitutes the novel feature of the present invention and the compounds which we

propose to use for this purpose are hydroxy derivatives of fuchsone or fuchsone-imonium dyes. The structure of fuchsone is as follows:

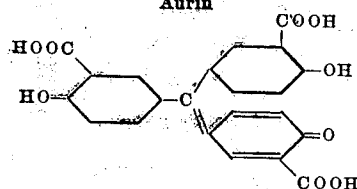


The hydroxy derivatives of fuchsone and the fuchsone-imonium dyes are well-recognized classes of dyes. Specific examples of compounds which we can use are as follows:

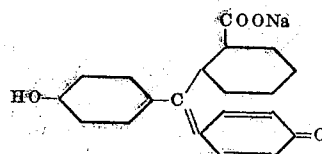
Hydroxy derivatives of fuchsone



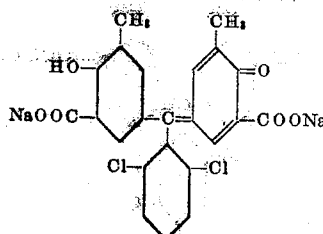
Aurin



Aurin tricarboxylic acid Schulz No. 846

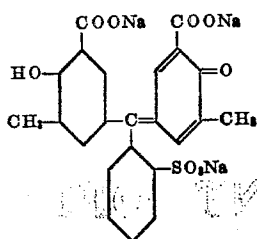


Phenolphthalein, sodium salt

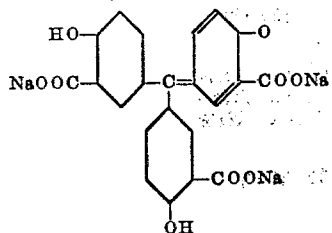


Eriochrome Azarol B Schulz No. 838

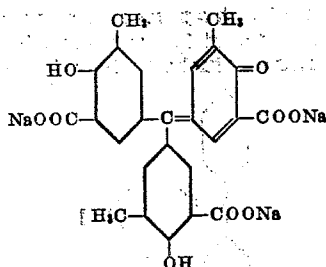
3



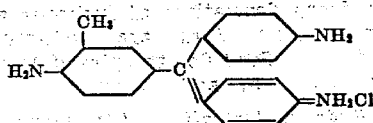
Eriochrome Cyanine RC Schulz No. 840



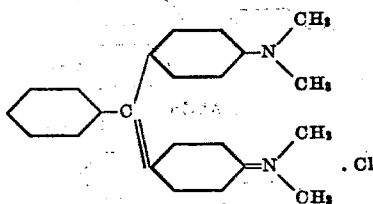
Aurin tricarboxylic acid Schulz No. 846 (Na salt)



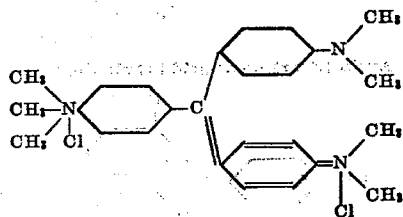
Eriochrome Geranol B Schulz No. 849

Fuchsone-imonium dyes

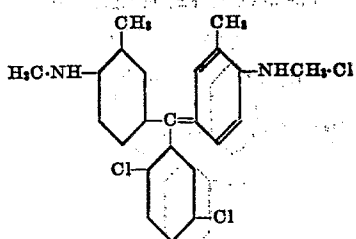
Basic Fuchsone RFN



Malachite green

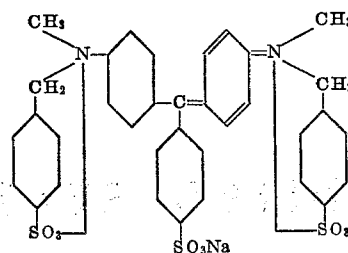


Methyl green

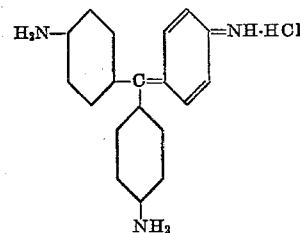


Acronol Brilliant Blue Schulz No. 761

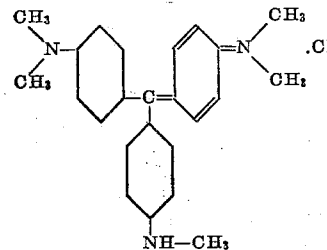
4



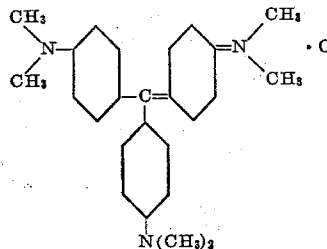
Light Green SFA Conc. Schulz No. 763



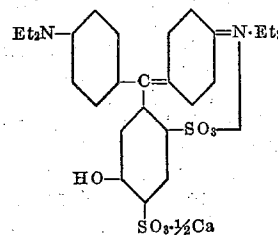
Pararosanine Hydrochloride Schulz No. 779



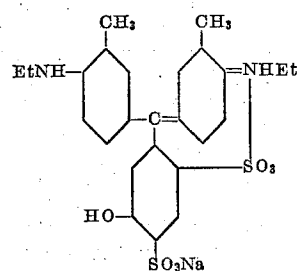
National Methyl Violet 2B conc. Schulz No. 783



Crystal Violet Schulz No. 785



Patent Blue VF Extra Conc. Schulz No. 826



Xylene Cyanol FF extra Schulz No. 828

70 The photographic emulsion used in the process of our invention is a gelatino silver halide emulsion such as a silver bromide emulsion, a silver bromoiodide emulsion, or a silver chloroiodide emulsion. It need not contain optical sensitizing dyes, although certain sensitizing dyes may

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be added to it for the purpose of inducing aerial fog, as explained more fully in Fallesen application, Serial No. 780,405. A suitable emulsion is that known as Burton's emulsion, described in Wall, "Photographic Emulsion," 1929, pages 52 and 53. Burton's emulsion is made as follows:

A. Silver nitrate-----g--	100
Water -----cc--	500
Ammonia—to form clear solution.	
B. Potassium bromide -----g--	80
Potassium iodide -----g--	50
Soft gelatin -----g--	20
Water -----cc--	1000
C. Dry gelatin -----g--	250

B is heated to 70° C. and A, cold, added to B with constant shaking, digested for 20 minutes at 50° C., and allowed to cool slowly. C is added after being allowed to swell for 20 minutes in water, drained, and melted. The emulsion is then set and washed.

An "internal latent image" emulsion, that is, one which forms the latent image mostly inside the silver halide grains, as described on pages 296 and 297 of Mees "The Theory of the Photographic Process," 1942, is especially useful for the process of my invention.

Most of the "internal latent image" emulsions are silver bromo-iodide emulsions of high iodide content, preferably containing at least 10%–20% of iodide. Burton's emulsion is an emulsion of this type, having a silver iodide content of approximately 40% of the content of silver halide. It is not absolutely essential, however, for the emulsion to contain silver iodide.

An "internal latent image" emulsion made as described in Davey and Knott U. S. application, Serial No. 790,232, filed December 6, 1947, now abandoned, may also be used according to my invention. This emulsion is prepared by first forming in the absence of ammonia and in one or more stages silver salt grains consisting at least partly of a silver salt which is more soluble in water than silver bromide, subsequently converting the grains to silver bromide or silver bromoiodide, and if the silver iodide content of the emulsion is less than 6% calculated on the total silver halide, treating such grains with an iodine compound to bring the silver iodide up to at least 6%, ripening preferably in the absence of ammonia and then either washing out some of the soluble salts or washing out the whole of the soluble salts, followed by the addition of soluble salts such as soluble chloride or bromide. An example of an emulsion made in this way is as follows:

Solution No. 1

Inert gelatin -----grams--	20	} at 40° C.
KCl -----do-----	20	
Water -----cc-----	560	

Solution No. 2

KCl -----grams--	100	} at 45° C.
Water -----cc-----	520	

Solution No. 3

AgNO ₃ -----grams--	195	} at 45° C.
Water -----cc-----	520	

Solution No. 4

KBr -----grams--	160	} at 45° C.
KI -----do-----	40	
Water -----cc-----	500	

Run solutions Nos. 2 and 3 simultaneously into

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solution No. 1 in a vessel, taking 90 seconds to do this. Then ripen for 1 minute at 45° C. Next add solution No. 4 then ripen for 20 minutes at 45° C. Next add 235 grams of inert gelatin (dry). Then ripen at 45° C. for 15 minutes during which time the gelatin dissolves. Set and shred the emulsion and then wash until free from all soluble bromide and then add about 150 cc. of 10% solution of KCl (by weight), and then add water to make 3½ litres.

An "internal latent image" type of silver halide emulsion may be defined as one which, when a test portion is exposed to a light intensity scale for a fixed time between 1/100 and 1 second, and developed for 4 minutes at 20° C. in the ordinary, "surface" developer (Example 1), exhibits a maximum density not greater than 1/5 the maximum density obtained when the same emulsion is equally exposed and developed for 3 minutes at 20° C. in an "internal" type developer (Example 2). Preferably the maximum density obtained with the "surface" developer is not greater than 1/10 the maximum density obtained when the same emulsion is developed in the "internal" type developer. Stated conversely, an "internal latent image" emulsion, when developed in an "internal" type developer (Example 2) exhibits a maximum density at least 5, and preferably at least 10, times the maximum density obtained when the same emulsion is exposed in the same way and developed in a "surface" developer (Example 1).

The developer used in the method of our invention should be one which produces oxidation fog or aerial fog. Such developers have been described by Dundon and Crabtree in "American Photography," 1924, vol. 18, page 742. An example of such a developer is a hydroquinone developer containing little or no sulfite, and is illustrated in Example 3.

The "aerial fog" may be produced in the developer in various ways and may be accelerated or intensified by resorting to various expedients. The developer used should preferably have low sulfite ion content and should preferably contain no silver halide solvent more powerful (as a silver halide solvent) than sulfite. Aerial fog may also be increased by bubbling air vigorously through the developer in such manner that the air comes frequently into contact with the emulsion surface of the photograph during development. Certain chemical agents such as copper sulfate incorporated either in the developer or in the emulsion itself may be used to produce or encourage the production of aerial fog. Hydrogen peroxide or certain dyes such as methylene blue increase aerial fog. Fogging agents containing labile sulfur are, however, unsuitable. The fogging action should produce developable surface latent image in the unexposed silver halide grains as explained in the Fallesen patent application Serial No. 780,405.

The developers of Stauffer U. S. application Ser. No. 780,569 contain heterocyclic nitrogen containing ring compounds having 5 or 6 atoms in the heterocyclic ring and are so constituted as to increase the maximum density of the positive image obtained in developing solutions capable of producing aerial fog. Typical compounds used in such developers are benzotriazole, methyl benzo triazole, 5-nitroindazole and 6-nitrobenzimidazole.

In general, the hydroxy derivatives of fuchsone or the fuchsone-imonium dyes are used in these developers in amounts of from 0.0005 to 0.05 per

liter of developer. In some cases, more or less than these amounts for example, from 0.00005 to 1, can be used. The amounts which are satisfactory for the various dyes listed above are shown in the following table. In each case the range is stated in grams of dye per liter of developing solution.

Hydroxy derivatives of fuchson

Dye	Range	Preferred
Aurin.....	.01-1	.2-.4
Phenolphthalein.....	.005-.04	.02
Eriochrome Azurol B.....	.001-.05	-----
Eriochrome Cyanine RC.....	.001-.02	-----
Eurin tricarboxylic acid (Na salt).....	.001-.1	-----
Eriochrome Geranol R.....	.001-.1	-----

Fuchson-imonium dyes

Dye	Range	Preferred
Basic Fuchsin RFN.....	.0005	-----
Malachite green.....	.0005-.032	-----
Methyl green.....	.00005-.0064	-----
Acrinol Brilliant Blue.....	.001-.01	-----
Light Green SFA Conc.....	.001-.05	.01
Pararosaniline Hydrochloride.....	.001-.02	-----
National Methyl Violet 2B conc.....	.001-.01	.002
Crystal Violet.....	.001-.01	.002
Patent Blue VS Extra Conc.....	.001-.005	-----
Xylene Cyanol FF extra.....	.001-.03	-----

An ordinary "surface type" developer, that is, one which develops an image only on the surface of the claims of "internal latent image" emulsions, is the following:

Example 1

p-Hydroxyphenylglycine ----- grams-- 10
Sodium carbonate (crystals) -----do----- 100
Water to -----liter-- 1
Development time, 4 min. at 20° C.

An "internal type" developer, that is, one which develops an image inside the grains of an "internal latent image" emulsion is the following:

Example 2

Hydroquinone ----- grams-- 15
Monomethyl-p-aminophenol sulfate -----do----- 15
Sodium sulfite (anhydrous) -----do----- 50
Potassium bromide -----do----- 10
Sodium hydroxide -----do----- 25
Sodium thiosulfate (crystals) -----do----- 20
Water to -----liter-- 1
Development times, 3 min. at 20° C.

Our invention will now be described by reference to the following specific examples.

Example 3

An exposure onto a direct positive photographic paper having an emulsion such as the Davey and Knott emulsion described above was made on a 1:1 optical printer by exposing for 30 seconds at f/11 and developing for 46 seconds in an open tray in a developer of the following composition:

Hydroquinone ----- grams-- 30
Sodium sulfite (des.) -----do----- 50
Paraformaldehyde -----do----- 12.5
Sodium hydroxide -----do----- 6
Benzotriazole -----do----- 2.5
Potassium bromide -----do----- 1
Basic Fuchsin RFN -----do----- 0.0005
Water to -----liter-- 1

This yielded a print of improved maximum density and lower minimum density than a similar

exposure processed 45 seconds in the same developer without the Basic Fuchsin RFN.

Example 4

A similar set of exposures to that of Example 3 was made on the same material by using additions of between 0.005 and 0.032 gram of Malachite Green per liter of developing solution. This was found to increase print contrast.

Example 5

A sensitive material such as that used in Example 3 was exposed in the same manner as in Example 3 and developed for 50 to 60 seconds in the same developer by using 0.01 to 1. gram per liter of sodium salt of aurin. This gave better quality prints than similar material developed in the same solution for 75 seconds at 70° F. without the dye in the developer.

Example 6

A similar set of exposures to that of Example 3 was made using from 0.00005 to 0.0064 gram of methyl green per liter of developer instead of Basic Fuchsin RFN. This was found to increase maximum density and decrease minimum density of the resulting image.

Example 7

A similar set of exposures to that of Example 3 was made using from 0.005 gram to 0.04 gram of phenolphthalein per liter of developer in place of Basic Fuchsin RFN. This served to lower the minimum density of the resulting images appreciably.

Example 8

The same emulsion as that used in Example 3 was exposed in the same way and developed in a developer of the following composition:

	Grams
Hydroquinone -----	10
Sodium sulfite (des.) -----	16
Paraformaldehyde -----	4
Sodium carbonate -----	25
Methyl benzotriazole -----	0.4
Aurin tricarboxylic acid (Na salt) -----	0.001
Water to 1 liter.	

Development of the exposed layer in this developer for times of 90 and 120 seconds showed an increase in maximum density of the resulting image.

It will be understood that the compounds and examples included herein are illustrative only and that the appended claims are to be taken as a measure of the invention.

What we claim is:

1. The method of obtaining a direct positive image in a silver halide emulsion layer, which comprises exposing to light rays to which the emulsion is sensitive, a silver halide emulsion layer a test portion of which upon exposure to a light intensity scale for a fixed time between 1/100 and 1 second and development for 3 minutes at 20° C. in the following internal type developer:

	Grams
Hydroquinone -----	15
Monomethyl-p-aminophenol sulfate -----	15
Anhydrous sodium sulfite -----	50
Potassium bromide -----	10
Sodium hydroxide -----	25
Sodium thiosulfate -----	20
Water to 1 liter.	

gives a maximum density at least 5 times the

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maximum density obtained when the equally exposed silver halide emulsion is developed for 4 minutes at 20° C., in the following surface developer (I):

p-Hydroxyphenylglycine	Grams 10
Sodium carbonate	100
Water to 1 liter.	

and developing the unexposed portion of said emulsion layer in a developing solution which produces aerial fog, and containing a heterocyclic, nitrogen-containing ring compound having at least 5 but not more than 6 atoms in the heterocyclic ring, and so constituted as to increase the maximum density of the positive image obtained in said developing solution which produces aerial fog, said developing solution also containing a small amount of a dye selected from the class consisting of hydroxy derivatives of fuchsone and fuchsone-imonium dyes.

2. The method of obtaining a direct positive image in a silver halide emulsion layer, which comprises exposing to light rays to which the emulsion is sensitive, a silver halide emulsion layer a test portion of which upon exposure to a light intensity scale for a fixed time between $1/100$ and 1 second and development for 3 minutes at 20° C. in the following internal type developer:

Hydroquinone	Grams 15
Monomethyl-p-aminophenol sulfate	15
Anhydrous sodium sulfite	50
Potassium bromide	10
Sodium hydroxide	25
Sodium thiosulfate	20
Water to 1 liter.	

gives a maximum density at least 5 times the maximum density obtained when the equally exposed silver halide emulsion is developed for 4 minutes at 20° C., in the following surface developer (I):

p-Hydroxyphenylglycine	Grams 10
Sodium carbonate	100
Water to 1 liter.	

and developing the unexposed portion of said emulsion layer in a developing solution which produces aerial fog, and containing a heterocyclic, nitrogen-containing ring compound having at least 5 but not more than 6 atoms in the heterocyclic ring, and so constituted as to increase the maximum density of the positive image obtained in said developing solution which produces aerial fog, said developing solution also containing a small amount of a hydroxy derivative of fuchsone.

3. The method of obtaining a direct positive image in a silver halide emulsion layer, which comprises exposing to light rays to which the emulsion is sensitive, a silver halide emulsion layer a test portion of which upon exposure to a light intensity scale for a fixed time between $1/100$ and 1 second and development for 3 minutes at 20° C. in the following internal type developer:

Hydroquinone	Grams 15
Monomethyl-p-aminophenol sulfate	15
Anhydrous sodium sulfite	50
Potassium bromide	10
Sodium hydroxide	25
Sodium thiosulfate	20
Water to 1 liter.	

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gives a maximum density at least 5 times the maximum density obtained when the equally exposed silver halide emulsion is developed for 4 minutes at 20° C., in the following surface developer (I):

p-Hydroxyphenylglycine	Grams 10
Sodium carbonate	100
Water to 1 liter.	

and developing the unexposed portion of said emulsion layer in a developing solution which produces aerial fog, and containing a heterocyclic, nitrogen-containing ring compound having at least 5 but not more than 6 atoms in the heterocyclic ring, and so constituted as to increase the maximum density of the positive image obtained in said developing solution which produces aerial fog, said developing solution also containing a small amount of fuchsone-imonium dye.

4. The method of obtaining a direct positive image in a silver halide emulsion layer, which comprises exposing to light rays to which the emulsion is sensitive, a silver halide emulsion layer a test portion of which upon exposure to a light intensity scale for a fixed time between $1/100$ and 1 second and development for 3 minutes at 20° C. in the following internal type developer:

Hydroquinone	Grams 15
Monomethyl-p-aminophenol sulfate	15
Anhydrous sodium sulfite	50
Potassium bromide	10
Sodium hydroxide	25
Sodium thiosulfate	20
Water to 1 liter.	

gives a maximum density at least 5 times the maximum density obtained when the equally exposed silver halide emulsion is developed for 4 minutes at 20° C., in the following surface developer (I):

p-Hydroxyphenylglycine	Grams 10
Sodium carbonate	100
Water to 1 liter.	

and developing the unexposed portion of said emulsion layer in a developing solution which produces aerial fog, and containing approximately 2.5 grams per liter of benzotriazole and also containing a small amount of a hydroxy derivative of fuchsone.

5. The method of obtaining a direct positive image in a silver halide emulsion layer, which comprises exposing to light rays to which the emulsion is sensitive, a silver halide emulsion layer a test portion of which upon exposure to a light intensity scale for a fixed time between $1/100$ and 1 second and development for 3 minutes at 20° C. in the following internal type developer:

Hydroquinone	Grams 15
Monomethyl-p-aminophenol sulfate	15
Anhydrous sodium sulfite	50
Potassium bromide	10
Sodium hydroxide	25
Sodium thiosulfate	20
Water to 1 liter.	

gives a maximum density at least 5 times the maximum density obtained when the equally exposed silver halide emulsion is developed for 4

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minutes at 20° C., in the following surface developer (I):

	Grams
p-Hydroxyphenylglycine	10
Sodium carbonate	100
Water to 1 liter.	

and developing the unexposed portion of said emulsion layer in a developing solution which produces aerial fog, and containing approximately 2.5 grams per liter of benzotriazole and also containing a small amount of a fuchsone-imonium dye.

6. The method of obtaining a direct positive image in a silver halide emulsion layer, which comprises exposing to light rays to which the emulsion is sensitive, a silver halide emulsion layer a test portion of which upon exposure to a light intensity scale for a fixed time between $\frac{1}{100}$ and 1 second and development for 3 minutes at 20° C. in the following internal type developer:

	Grams
Hydroquinone	15
Monomethyl-p-aminophenol sulfate	15
Anhydrous sodium sulfite	50
	25

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Potassium bromide	10
Sodium hydroxide	25
Sodium thiosulfate	20
Water to 1 liter.	

5 gives a maximum density at least 5 times the maximum density obtained when the equally exposed silver halide emulsion is developed for 4 minutes at 20° C., in the following surface developer (I):

	Grams
p-Hydroxyphenylglycine	10
Sodium carbonate	100
Water to 1 liter.	

15 and developing the unexposed portion of said emulsion layer in a developing solution which produces aerial fog, and containing approximately 0.4 gram per liter of methyl benzotriazole and also containing a small amount of a hydroxy derivative of fuchsone.

20 ROBERT ELIOT STAUFFER.
JOHN SPENCE.

No references cited.

Certificate of Correction

Patent No. 2,490,758

December 6, 1949

ROBERT ELIOT STAUFFER ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 3, line 59, next to last formula, right-hand portion thereof, after "CH₃" insert +ZnCl₂;

and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 18th day of April, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.