United States Patent Office 3,418,123 Patented Dec. 24, 1968



3,418,123

# INTENSIFICATION PROCESS UTILIZING SUPERPOSED SILVER HALIDE LAYERED STRUCTURE

Eugene Frederick Haugh, Old Bridge, N.J., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Filed Oct. 22, 1965, Ser. No. 502,419
7 Claims. (Cl. 96—63)

## ABSTRACT OF THE DISCLOSURE

Process for forming images comprising (1) imagewise exposing an outer silver iodobromide stratum of an element, (2) developing said stratum in contact with an inner silver chloride or silver chlorobromide layer to form a precursory image in said inner layer, (3) developing said precursory image in the presence of an antifogging agent and (4) fogging the silver chloride or silver chlorobromide layer prior to completion of the second developing step wherein a secondary image in the inner layer is formed in registration with the primary silver image in the outer stratum.

This invention relates to photography and more particularly to a new process for the intensification of a silver image.

It is known that intensification of a silver image, to improve the speed, contrast, and maximum density characteristics, can be effected by various means. Improvements in speed are often obtained by adding sensitizing materials to the emulsion, normally with an accompanying increase in photographic fog. The most common means of increasing contrast and maximum density is by an increase in silver halide coating weight, with an accompanying increase in the cost of manufacture.

An object of the present invention is to improve the speed, contrast, and maximum density of silver images. A further object is to effect these improvements without appreciable increases in photographic fog and with the use of normal or even lower than normal coating weights of silver halide. Still further objects will be apparent from the following description of the invention.

The above objects are attained in accordance with the process of this invention which comprises:

(a) forming a precursory image in a water-permeable layer of silver chloride or silver chlorobromide crystals of relatively small grain size and of low sensitivity to actinic radiation by developing in an aqueous developer solution an adjacent water-permeable stratum in operative association therewith, said stratum

(1) being imagewise exposed to actinic radiation,

(2) containing silver iodobromide crystals of 1 to 10 mole percent silver iodide, said crystals being of relatively large grain size, their average diameter being at least two times that of the silver chloride or silver chlorobromide crystals and having high sensitivity to actinic radiation;

(b) developing said precursory image in an aqueous developer in the presence of at least one antifogging agent (e.g., 0.1 to 3, or preferably 0.5 to 1.5 g. of said agent per liter of developer solution) which renders the silver chloride or chlorobromide crystals undevelopable in said second developer solution in areas not adjacent to exposed and developed silver iodobromide crystals and, prior to completion of the second developing step, fogging the silver halide crystals in said layer. The developed element can then be fixed.

Preferably, the silver iodobromide crystals have an average diameter at least three times that of the silver chloride or chlorobromide crystals.

The above two types of silver halide crystals must be in separate but adjacent strata. In manufacturing photographic elements suitable for the process of this invention, the silver halide crystals may be coated as separate emulsion layers on a single support or coated on separate supports. In the latter case, the coated emulsion layers containing the two types of silver halide crystals must be brought together in intimate contact during the first development step of this invention.



In the preferred embodiment, wherein two emulsion strata are applied to a single support, the support is first coated with a gelatino-silver chloride or chlorobromide photographic emulsion having a relatively small crystal size and containing a hardening agent. This emulsion should contain from 50 to 100 mole percent silver chloride and from 50 to 0 mole percent silver bromide. Optionally, a thin gelatin separator layer may be applied over the silver chloride or chlorobromide emulsion layer. Then there is coated a gelatino-silver iodobromide emulsion layer containing relatively large silver iodobromide crystals. The iodobromide emulsion should comprise from 1 to 10 mole percent silver iodide (preferably from 3 to 6%) and be considerably more sensitive to actinic radiation than the silver chloride or chlorobromide emulsion. A thin gelatin antiabrasion layer may, if desired, be applied over the iodobromide emulsion layer.

A typical processing operation involves imagewise exposure at a light intensity suitable for forming a latent image in the faster, outer silver iodobromide emulsion layer (but with insufficient light to expose appreciably the inner silver chloride or chlorobromide emulsion layer). The element is then subjected to a first development in a silver halide developer solution. It is then fogged by a light exposure during a second development using a developer solution containing an antifoggant effective for silver chloride or chlorobromide but not for silver iodide. This produces an image in the silver chloride or chlorobromide layer corresponding to that in the iodobromide layer. Finally, the element is fixed, washed and dried in a conventional manner. The silver iodobromide emulsion may be removed by washing it in warm water after the first development if this emulsion as coated is free from hardening agents. After considerable aging, the iodobromide emulsion will become hardened due to migration of hardening agents from the silver chloride or chlorobromide emulsion layer. However, it has been found that separation of the two layers is not essential to the process of this invention if the antifoggant is also effective for the iodobromide crystals. In fact, there is an advantage in not separating the layers since higher density images can be obtained when both layers contribute to the image.

During the processing, it is believed that iodide ions liberated by developing silver iodobromide migrate to nearby silver chloride or chlorobromide grains and deposit on their surfaces to form the precursory image. The deposition of iodide ions affects the developability of the silver chloride, chlorobromide, or iodobromide crystals during the second development by preventing the action of the antifoggant. Thus, silver chloride or chlorobromide crystals are reduced to form a metallic silver image in areas corresponding to the image developed in the silver iodobromide emulsion. And, where the outer layer is not washed off, the two silver images reinforce one another to afford maximum utilization of the silver halide in the element.

Alternately, the process of this invention may be carried out with elements having separate supports for the two types of emulsion layers described above. Each of the emulsion layers may optionally be overcoated with thin antiabrasion layers. In this embodiment, the faster film (the silver iodobromide) is exposed imagewise and then developed in emulsion-to-emulsion contact with the

slower film (silver chloride or chlorobromide) by spreading a thin layer of developer between the two films. After development, the films are separated and processing of the slower film is continued with light-fogging exposure during second development, fixing and (optionally) one or more washing steps. The second development requires the use of an antifoggant-containing developer which restricts development to those areas where were in contact during first development with developing (i.e., exposed) areas of the faster film. In this embodiment, wherein the two different emulsion layers are on separate supports, proper control of the first development makes it desirable to use a special processing machine whereby uniform application of developer solution between the two films can be attained. Also it is desirable to maintain very accurate control of developer viscosity and composition and of processing times.

The invention will be further illustrated but is not intended to be limited by the following examples:

## EXAMPLE I

A gelatino-silver chloride fine grain emulsion of the relatively low speed lithographic type was applied at a coating weight of about 23 mg./dm.$^2$ of silver on a suitably subbed, 0.005-inch thick cellulose acetate photographic film base. After drying, the emulsion layer was overcoated with a separator solution to form a coating of approximately 5 mg./dm.$^2$ of gelatin hardened with chrome alum. The separator layer was then dried and overcoated with a high speed, large grain gelatino-silver iodobromide emulsion of the medical X-ray type comprising 4.5 mole percent silver iodide and 5.5 mole percent silver bromide, applied at a coating weight of about 45 mg./dm.$^2$ of silver. Finally, an antiabrasion solution was applied at a coating weight of approximately 5 mg./dm.$^2$ of gelatin hardened with an aldehyde type hardening agent.

A sample of this film was exposed through a Corning filter No. 5850 (2.6 mm. thick), a neutral density 0.3 filter, and a square-root-of-two sensitometric step wedge in a Positive 1B Sensitometer using a 500-watt lamp operating at 3.38 amps, for 0.08 second at a distance of 82 inches. This manner of exposure to light is essentially that of the "American Standard Method for the Sensitometry of Medical X-ray Film." (PH2.9–1956).

The exposed strip was processed with all solutions at 68° F., beginning with development for 5 min. in a first developer solution of the following composition:

### FIRST DEVELOPER

| | | |
|---|---|---|
| Water at 100° F. | ml. | 500 |
| Sodium sulfite, anhyd. | g. | 59.0 |
| Sodium metaborate octahydrate | g. | 12.0 |
| Sodium hydroxide | g. | 7.8 |
| N-methyl-p-aminophenol hydrosulfate | g. | 4.7 |
| Hydroquinone | g. | 11.0 |
| Potassium bromide | g. | 3.8 |
| Potassium chloride | g. | 0.5 |
| Sodium acetate | g. | 5.7 |

Water to make 1.0 liter.

This was followed by a one-minute wash in running water and then a three-minute treatment in a second developer solution of the following composition:

### SECOND DEVELOPER

| | | |
|---|---|---|
| Water | ml. | 800 |
| $Na_2SO_3$, anhyd. | g. | 45 |
| Hydroquinone | g. | 8.0 |
| $NaBO_2 \cdot 4H_2O$ | g. | 32.0 |
| NaOH | g. | 8.0 |
| NaBr | g. | 1.0 |
| NaCl | g. | 22.0 |
| 1% by weight 2-mercapto - thiazoline in ethanol | ml. | 130 |
| Benzotriazole, 10% by wt. aqueous solution | ml. | 20 |

Water to 1000 ml.

After 30 seconds in the second developer, an overhead room light was turned on for 5 seconds to provide an over-all or flash exposure, without removing the strip from the developer solution. The exposing light was a dual 40-watt white fluorescence fixture bulb at a distance of 64 inches. Exposure was through the back since the strip was emulsion side down in a shallow developer tray, about ¾ inch below the surface of the liquid. After exposure, development was continued in the dark until the full three minutes of second development had elapsed.

Next, the strip was treated for 10 seconds in an acid stop bath (40 ml. glacial acetic acid in a liter of water) and then fixed for 5 minutes in the following solution:

### FIXER SOLUTION

| | | |
|---|---|---|
| Water | ml. | 600 |
| $Na_2S_2O_3$, anhyd. | g. | 153 |
| $Na_2SO_3$, anhyd. | g. | 15 |
| Borax | g. | 18 |
| Glacial acetic acid | ml. | 12 |
| Potassium alum | g. | 20 |

Water to 1000 ml.

Fixing was followed by washing for 10 minutes in running water and drying in air at room temperature.

As a control, a commercial medical X-ray film, coated on both sides of the support to a total coating weight of 125 mg./dm.$^2$ of silver, was exposed on both sides with the same sensitometric exposure which had been used only on one side of the experimental film. The control was processed in the same manner except for elimination of the second development and second exposure steps. Sensitometric advantages of the experimental film can be seen from the following data:

| | Fog | $\gamma$ | Speed* |
|---|---|---|---|
| Experimental film | .17 | 3.50 | 8.2 |
| Control | .20 | 2.94 | 7.1 |

*Inertia speed in terms of step number when sensitometric results are plotted on K & E No. 56–62 paper and the exposure is as described above.

## EXAMPLE II

The gelatino-silver halide emulsions of Example I were coated on separate supports of the same cellulose acetate film base used in Example I. The silver chloride emulsion was applied at a coating weight of about 29 mg./dm.$^2$ of silver to form an image receptor film while the silver iodobromide emulsion was applied at about 29 mg./dm.$^2$ of silver. No gelatin overcoats were applied.

An apparatus was constructed for processing these films with a viscous developer. The apparatus consisted of the following four main parts:

(1) The extruder was a mounted 100 ml. hypodermic syringe containing the viscous developer with the plunger propelled by a variable speed motor-driven screw. The motor was geared to deliver developer at the rate of from 18.5 to 20 ml. per minute. Uniform, nonpulsating flow was thus provided.

(2) The extrusion die was a wedge shaped polymethylmethacrylate plastic device, with guide slots, top and bottom, for 35-mm. film strips. Synthetic rubber tubing, cemented into the back of the die, connected it to the extruder. The unadjustable lip opening was approximately eight thousandths of an inch in the smallest dimension.

(3) Two high precision metering rolls of identical diameters were geared to rotate in opposite directions. Their separation was adjustable in marked increments of .0004 inch. Film 10 inches wide could be accommodated and the roller speed varied from 223 to 384 cm./min. The satin chrome finish on the rolls provided sufficient grip to feed both strips through the metering and spreading gap without slipping.

(4) The sequencer contained four microswitches and four adjustable motor driven timing cams. It was set to

start and stop both extruder and metering rolls at the appropriate time. The operation sequence was:

Started by push button.
Extruder started delivering developer between positioned strips.
About 1½ seconds later the metering rolls started pulling the strips.
About 2 seconds later the extruder stopped.
About 2 seconds later the sandwich was delivered and the rolls stopped.

The limited speed variation was provided by variable transformers in both rolls and extruder circuits.

Ten-inch by 35-mm. strips of the two films described above were cut from the coatings and the silver iodobromide strip was given a sensitometric exposure as described in Example I. This exposed film strip and an unexposed strip of the silver chloride film were rolled into the above processing apparatus (emulsion side to emulsion side) with simultaneous injection of viscous developer between the emulsion surfaces and the remainder of the above "operation sequence" carried out. The viscous developer was prepared as follows:

| | | |
|---|---|---|
| Distilled water | ml. | 700 |
| Hydroxyethyl ether of cellulose [1] | g. | 20 |

[1] Nonionic, water-soluble, rapid dissolving ether—2% aqueous solution has viscosity of 4500–6500 cps. on Brookfield viscometer at 25° C. ("Natrosol"® MR—Hercules Powder Co.)

Stir till smooth. Add 1 drop NaOH(3N). Stir till completely homogeneous and add:

| | | |
|---|---|---|
| Sodium sulfite | gm. | 26.66 |

Mix separately:

| | | |
|---|---|---|
| Diethylene glycol monomethylether | ml. | 15 |
| Distilled water | ml. | 150 |
| Sodium sulfite, anhyd. | gm. | 3.33 |
| Hydroquinone | gm. | 50.0 |

Stir. When dissolved, add separate mixture slowly to viscous solution. Then add:

| | | |
|---|---|---|
| Sodium carbonate (anhyd.) | gm. | 35.0 |
| Sodium hydroxide | gm. | 17.2 |

pH=11.00±0.05.

Upon completion of the "operation sequence," the "delivered" sandwich was retained in the apparatus so that development could proceed for a total of 2 minutes. The films were then separated and washed in running tap water for 2 minutes. The silver chloride receptor film was placed in the second developer solution described in Example I.

After 2 seconds in the second developer, the film was given an overall flash exposure with a photo-flood lamp (Photo DXC —3400° K., 500-watts, 15-volts) for 15 seconds at a distance of 9 inches of air and through ¼ inch of the developer solution. After the flash exposure the development was continued for 1 minute and 43 seconds to make a total of 2 minutes in the second developer solution. Next, the film was placed in an acetic acid short stop for 30 seconds, was rinsed 10 seconds in tap water, fixed for 5 minutes in the fixing solution of Example I, washed in water for 10 minutes, and dried. The resultant image in the receptor film was a high contrast copy of the original low contrast image which formed in the silver iodobromide film. As a control, a commercial medical X-ray emulsion coated on only one side of the support to a total coating weight of about 63 mg./dm.$^2$ of silver, was given an identical exposure and then processed according to the manufacturer's recommendations. Sensitometric curves were drawn for the two films and it was seen that the experimental film of the present invention was about 6 times as fast as the control, had a gamma of 57% of the control, higher top density, and a longer straight line portion of the curve.

## EXAMPLE III

A photographic film was prepared similar to that described in Example I except that the silver iodobromide emulsion contained 4.0 mole percent silver iodide (instead of 4.5%) and the gelatin was unhardened. The silver chloride emulsion and the silver iodobromide emulsion were applied at coating weights, respectively, of 29 and 43 mg./dm.$^2$ of silver.

Two samples of this film were given a sensitometric exposure as in Example I and a first development in a conventional photographic developer solution containing hydroquinone and p-methylaminophenol sulfate. After a one-minute water wash, one of the samples was treated with a second developer solution containing the antifoggant 5-nitrobenzimidazole nitrate for a total of 3 minutes. After 30 seconds in the second developer, room lights were turned on for 15 seconds to provide a fogging exposure. The image of this sample was definitely intensified in comparison with the control sample which received no treatment in the second developer. The formulation of the second developer was as follows:

| | | |
|---|---|---|
| $Na_2SO_3$ (anhyd.) | g. | 80 |
| Hydroquinone | g. | 16 |
| Boric Acid | g. | 5.5 |
| KBr | g. | 10 |
| 5-Nitrobenzimidazole nitrate, 2% by weight ethanol soln. | ml. | 75 |
| NaOH | g. | 24 |

$H_2O$ to 1000 ml.

## EXAMPLE IV

Five samples of the film of Example III were given an exposure, first development, and one-minute wash as in that example. Two of the samples were then given a second development for three minutes which included the 15-second fogging exposure of Example III. The second developer composition comprised a mixture of Solution A and one or more solutions of antifoggants as indicated below.

### SOLUTION A

| | Grams |
|---|---|
| $Na_2SO_3$ (anhyd.) | 100 |
| Hydroquinone | 20 |
| NaOH | 40 |
| NaBr | 2 |
| NaCl | 50 |

$H_2O$ to 2000 ml.

### SECOND DEVELOPER COMPOSITION

*Sample 1 (control).*—No second development.
*Sample 2.*—500 ml. Solution A+40 ml. of 1% by weight ethanol solution of 1-phenyl-5-mercaptotetrazole.
*Sample 3.*—Same as for Sample 2+10 ml. of 10% by weight ethanol solution of benzotriazole.
*Sample 4.*—900 ml. Solution A+54 ml. of a 1% by weight ethanol solution of 2-mercaptobenzothiazole+20 ml. of a 10% by weight ethanol solution of benzothiazole.
*Sample 5.*—900 ml. Solution A+63 ml. of a 1% by weight ethanol solution of 2-benzoxazolethiol.

Sample 2 had a highly intensified image (compared to the control) but with appreciable increase in fog level. Sample 3 was intensified to lesser degree but there was no discernible increase in fog over that of the control. Samples 4 and 5 had good image intensification along with some fog.

In a similar experiment but using somewhat different developer solutions, it was found that 2-mercapto-4-phenylthiazole was also quite an effective antifoggant in the second developer for image intensification according to the present invention.

## EXAMPLE V

The silver iodobromide emulsion of Example III was coated on the film base of Example I without an antiabrasion overcoating. Another web of the same film base was coated with a silver chlorobromide emulsion of the fine grain, lithographic type having 70 mole percent silver bromide. This emulsion had an unusually low concentration of gelatin binder, i.e., only 10 g. of gelatin per mole of silver halide.

A sample of the silver iodobromide coating was exposed as in Example I, placed in contact (emulsion side to emulsion side) with a sample of the silver chlorobromide coating, and given a conventional first development with a high pH hydroquinone developer solution. The films were then peeled apart and the silver chlorobromide film was washed and placed in the following second developer solution for three minutes under ordinary (white light) room illumination:

SECOND DEVELOPER SOLUTION

| | | |
|---|---|---|
| $Na_2SO_3$ (anhyd.) | g. | 50 |
| Hydroquinone | g. | 10 |
| NaOH | g. | 20 |
| NaBr | g. | 5 |
| KCl | g. | 20 |
| Benzotriazole, 10% by weight solution in ethanol | ml. | 100 |
| 2-Mercapto-4-phenylthiazole, 1% by weight solution in ethanol | ml. | 100 |

Water to 1200 ml.

The image formed in the silver chlorobromide film represented a substantially intensified reproduction of the originally developed image in the silver iodobromide film.

## EXAMPLE VI

Three sample strips of the two-layer film of Example III were exposed, given a first development, and washed as described in that example. The strips were then given a second development for 3 minutes in the developers described below, an acid stop treatment, and were fixed, washed and dried. Safelights were used throughout the processing.

CONTROL SECOND DEVELOPER

| | | |
|---|---|---|
| Water | ml. | 800 |
| $Na_2SO_3$ (anhyd.) | g. | 45 |
| Hydroquinone | g. | 8 |
| NaOH | g. | 17 |
| NaBr | g. | 1 |
| NaCl | g. | 22 |
| 2-Mercaptothiazoline, 1% by weight solution in ethanol | ml. | 130 |
| Benzotriazole, 10% by weight solution in ethanol | ml. | 9 |

Water to 1000 ml.

The three strips were treated in the following solutions for second development:

SECOND DEVELOPER SOLUTION

Strip 1 500 ml. control second developer.

Strip 2 500 ml. control second developer+1 g. hydrazine hydrochloride.

Strip 3 500 ml. control second developer+3 g. semicarbazide hydrochloride.

Strip No. 1, the control showed no signs of intensification in the absence of a fogging exposure to white light. Strips No. 2 and No. 3 both showed good intensification along with very little increase in fog. Thus it was found that both hydrazine and semicarbazide are effective chemical fogging agents which can be substituted for the light fogging used in the earlier examples.

The high speed photographic emulsion useful for forming the primary image, i.e., the image formed by the first exposure, must be of the silver iodobromide type such as used in high speed negative or in X-ray formulations.

The fine grain, slow emulsions useful in the image receptive layer can be selected from the pure silver chlorides and from silver chlorobromide emulsions. Useful emulsion types for the slower layer can be direct positive, litho, and special Lippmann type silver chloride emulsions of extremely small grain size.

The emulsions, particularly the high speed emulsions, may contain sensitizing dyes and/or sensitizers containing labile sulfur, e.g., allyl isothiocyanate, allyl diethyl thiourea, phenyl isothiocyanate and sodium thiosulfate; the polyoxyalkylene ethers in Blake et al., U.S. Patent 2,400,532, and the polyglycols disclosed in Blake et al. U.S. Patent 2,423,549. Other non-optical sensitizers such as amines as taught by Staud et al., U.S. Patent 1,925,508 and Chambers et al., U.S. 3,026,203, and metal salts as taught by Baldsiefen U.S. Patent 2,540,086 may also be used.

In place of gelatin other natural or synthetic water-permeable organic colloid binding agents can be used. Such agents include water permeable or water-soluble polyvinyl alcohol and its derivatives, e.g., partially hydrolyzed polyvinyl acetates, polyvinyl ethers, and acetals containing a large number of extralinear —$CH_2CHOH$— groups; hydrolyzed interpolymers of vinyl acetate and unsaturated addition polymerizable compounds such as maleic anhydride, acrylic and methacrylic acid ethyl esters, and styrene. Suitable colloids of the last mentioned type are disclosed in U.S. Patents 2,276,322, 2,276,323 and 2,347,811. The useful polyvinyl acetals include polyvinyl acetalaldehyde acetal, polyvinyl butyraldehyde acetal and polyvinyl sodium o-sulfobenzaldehyde acetal. Other useful colloid binding agents include the poly-N-vinyllactams of Bolton U.S. Patent 2,495,918, the hydrophilic copolymers of N-acrylamido alkyl betaines described in Shacklett U.S. Patent 2,833, 650 and hydrophilic cellulose ethers and esters.

The above binders, preferably gelatin, are useful not only in the emulsion but in various auxiliary layers such as subs, overcoatings, and backings.

The film support for the emulsion layers used in the novel process may be any suitable transparent plastic. For example, the cellulosic supports, e.g., cellulose acetate, cellulose triacetate, cellulose mixed esters, etc., may be used. Polymerized vinyl compounds, e.g., copolymerized vinyl acetate and vinyl chloride, polystyrene, and polymerized acrylates may also be used, as well as the film formed from the polyesterification product of a dicarboxylic acid and a dihydric alcohol made according to the teachings of Alles, U.S. Patent 2,779,684 and the patents referred to in the specification of that patent. Other suitable supports are the polyethylene terephthalate/isophthalates of British Patent 766,290 and Canadian Patent 562,672 and those obtainable by condensing terephthalic acid and dimethyl terephthalate with propylene glycol, diethylene glycol, tetramethylene glycol or cyclohexane 1,4-dimethanol (hexahydro-p-xylene alcohol). The films of Bauer et al., U.S. Patent 3,052,543 may also be used. The above polyester films are particularly suitable because of their dimensional stability.

The emulsions can contain known antifoggants, e.g., 5-nitrobenzimidazole, benzotriazole, triazaindenes, etc., as well as the usual hardeners, i.e., chrome alum, formaldehyde, dimethylol urea, mucochloric acid, etc. Other emulsion adjuvants that may be added comprise matting agents, plasticizers, toners, optical brightening agents, surfactants, image color modifiers, non halation dyes, etc.

In the first development step, the development reaction proceeds in a conventional manner and suitable results have been obtained with the use of conventional photographic developer solutions containing conventional photographic developing agents, e.g., hydroquinone, Metol, 1-phenyl-3-pyrazolidone, etc., and various combinations of these developing agents.

It is the second development step which is unique in the present invention since, according to the proposed mechanism, the second developer solutions should contain an antifoggant which is normally effective to protect silver chloride or silver chlorobromide crystals, but which protective action is prevented imagewise by iodide ions released from the adjacent layer during first development. Antifoggants which have been tested by inclusion in a second developer solution and found satisfactory for this specific purpose include 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 2-mercapto-4-phenylthiazole, 2-mercaptothiazoline, 5-nitrobenzimidazole nitrate, and 1-phenyl-5-mercaptotetrazole. The addition of benzotriazole as an auxiliary agent is particularly effective in the reduction of fog. Hydroquinone is the preferred agent for the second developer solution.

In most of the experimental work the emulsion was fogged by exposure to light during the second development. Limited tests, however, indicated that chemical fogging agents such as hydrazine or semicarbazide could be used in the second developer solution in lieu of a fogging exposure to light. In the embodiment of this invention wherein the two emulsions are coated on separate supports and brought together during the first development step, the developer solution for this step has the particular requirement that it contain a thickening agent, at least for use in the apparatus described in Example II. That example describes the preferred thickening agent but other useful thickening agents, include methyl cellulose, ethyl cellulose, polyvinyl alcohol, poly (methyl-vinyl ether) maleic anhydride, hydroxyethyl cellulose, sodium carboxylmethyl cellulose, and ethylene oxide polymers.

In manufacturing the photosensitive elements, the emulsions contain hardening agents such as chrome alum, dimethylol urea, formaldehyde, and mucochloric acid. The hardening agent may be in the photosensitive emulsion itself, in the adjacent gelatin layer, or in both. In the case of the two photosensitive emulsion layers being coated on a single support, gelatin separator and abrasion layers are optional and it has been found that satisfactory results may be obtained using either hardened or unhardened layers containing the iodobromide emulsion layer. The slower, fine grained silver chloride or silver chlorobromide emulsion is always hardened.

The present invention is concerned primarily with an improved photographic element for use in X-ray photography, especially medical X-ray photography where there is a constant desire to improve the sensitivity of the product so that satisfactory X-ray exposures may be made with a minimum of exposure of the patient. Other potential uses of the elements and processes of this invention may be found wherever there is a need for images of very high optical density without resorting to excessive coating weights of silver halide, e.g., in the field of Graphic Arts. Other uses can be envisioned wherein extremely high speed is required, i.e., where it is desired to form a photographic image under conditions of very low illumination.

A particular advantage of the embodiment of this invention described in Example I, in X-ray applications, resides in a structure having a silver chloride inner layer and with both emulsions coated on the same side of a single support. In practical use, this element would be exposed between two phosphor intensifying screens which convert an X-ray pattern to a pattern of short wave length visible light. Since the silver chloride emulsion layer is essentially transparent to much of the radiation emitted by the intensifying screens, this means that both screens are effective in exposing the silver iodobromide layer. In contrast, the control element of Example I is a conventional film having a silver iodobromide emulsion coated on both sides of the film base support. These emulsions are considerably more opaque to the emitted radiations of the intensifying screens so, in effect, each screen exposes the emulsion on just one side of the film base. Nearly twice as much exposing (visible) radiation is thus available for exposing the film elements of this invention without increasing the X-ray exposure.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

**1.** A process which comprises:

(a) forming a precursory image in a water-permeable layer of silver chloride or silver chlorobromide crystals of small grain size and of low sensitivity to actinic radiation by developing in an aqueous developer solution an adjacent water-permeable stratum in operative association therewith, said stratum

(1) being imagewise exposed to actinic radiation to form a latent image therein with light insufficient to expose appreciably the silver chloride or silver chlorobromide crystals, said stratum

(2) containing silver iodobromide crystals of 1 to 10 mole percent silver iodide, said crystals being of large grain size, their average diameter being at least two times that of the silver chloride or silver chlorobromide crystals and having having high sensitivity to actinic radiation;

(b) developing the precursory image in an aqueous developer in the presence of at least one antifogging agent which renders the silver chloride or chlorobromide crystals undevelopable in said second developer soluton in areas not adjacent to exposed and developed silver iodobromide crystals and, prior to completion of the second developing step, fogging the silver halide crystals in said layer.

**2.** A process according to claim **1** wherein the layer and stratum are in surface contact with each other.

**3.** A process according to claim **1** wherein the layer and stratum are separated by a very thin water-permeable colloid layer.

**4.** A process according to claim **1** wherein the layer and stratum contain gelatin as a binding agent for the silver halide grains.

**5.** A process according to claim **1** wherein the antifogging agent is 2-mercaptothiazoline.

**6.** A process according to claim **1** in which the fogging step is by means of actinic radiation.

**7.** A process according to claim **1** wherein the antifogging agent is in the second developer solution.

**References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 1,303,635 | 5/1919 | Capstaff | 96—68 |
| 656,751 | 8/1900 | Schwarz | 96—68 |
| 2,875,052 | 2/1959 | Weyde | 96—68 |
| 3,050,391 | 8/1962 | Thompson et al. | 96—61 |
| 3,072,480 | 1/1963 | Abbott et al. | 96—29 |
| 3,140,179 | 7/1964 | Russell | 96—68 |

NORMAN G. TORCHIN, *Primary Examiner.*

C. E. DAVIS, *Assistant Examiner*

U.S. Cl. X.R.

96—29, 50, 66.5, 68