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PROCESS FOR FORMING IMAGES AND ELEMENTS THEREFOR

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This invention relates to photography and more particularly to a process for forming images in exposed photographic silver halide layers and to photographic elements bearing such layers useful for providing high image covering power in a highly light-sensitive photographic element.

It has been disclosed in Capstaff, U.S. Patent 1,303,635, that a two-layer photographic film may be processed to yield an image in the upper layer which is subsequently used to modulate printing light to form an image of opposite sign in the lower emulsion. Luckey et al., U.S. Patent 2,996,382, discloses that iodide ion liberated during the development of a surface latent image in a silver bromoiodide emulsion migrates to some adjacent internally prefogged silver halide emulsion grains, either in the same or in an adjacent emulsion layer, to catalyze the development of said grains and thus intensify the original silver image. Although these references disclose secondary image formation, each of the processes requires a number of steps such as the second exposure to light in the former reference and the necessity of using internally prefogged silver halide in the latter.

It is an object of this invention to provide new photographic processes. Another object is to provide such processes that will yield improved photographic images having high covering power, i.e., high image density per unit weight of silver halide in the emulsion, without the sacrifice of photographic speed which is normally associated with high covering power images. A further object is to provide new photographic processes which make possible the more efficient utilization of the developed silver in a photographic image. Still further objects will be apparent from the following detailed description of the invention.

The novel process of this invention comprises:

(1) Subjecting to an imagewise exposure and thereby forming a latent image in the outer light-sensitive silver halide emulsion layer of a photographic element having, on a support, a contiguous inner emulsion layer comprising unfogged internal image silver halide grains and of such sensitivity that said imagewise exposure results in development of less than one-tenth (preferably less than one-twenty-fifth) of the available silver halide in the inner layer, the silver halides of both layers being dispersed in a water-permeable, macromolecular, organic colloid binding agent,

(2) Treating said outer layer with an aqueous photographic developer solution to form a visible silver image in said layer, and

(3) Not earlier than step (2), treating the outer layer of the element with an aqueous solution containing an anion, preferably iodide, capable of forming a silver salt which is more insoluble in water than the silver halide of either of the said emulsion layers, said anion diffusing imagewise differentially through the outer layer and forming in the inner layer, a silver salt image from said anion in register with the earlier formed silver image in the outer layer.

The inner emulsion layer containing unfogged internal image silver halide grains defined above is further characterized in that, upon development, it produces an optical density in unexposed areas (i.e., a fog density) less than one-tenth its maximum net image density, the development being carried out in an internal image developer containing a silver halide solvent, i.e., for 5 minutes at 65° F. in "Developer B" of U.S. 2,996,382, which has the following formula:

	Grams
N-methyl-p-aminophenol sulfate	2.0
Sodium sulfite, desiccated	90.0
Hydroquinone	8.0
Sodium carbonate, monohydrate	52.5
Potassium bromide	5.0
Sodium thiosulfate	10.0

Water to make 1 liter.

Additionally, the emulsion layer containing unfogged internal image silver halide grains may be defined as one which, at a coating weight of 540 mg./sq. ft. of silver (equivalent to 58.2 mg./dm.^{2}), will produce an optical density of less than 0.4 in unexposed areas when developed for 5 minutes at 65° F. in "Developer B" of U.S. 2,996,382.

The imagewise exposure is preferable to actinic radiation but can be effected by mechanical (e.g., pressure) or chemical means.

In a preferred embodiment of this invention, a photographic element having a high speed, large grain photographic silver halide emulsion of relatively low covering power is coated over a lower speed, fine grain unfogged (as defined above) silver halide emulsion of high covering power and is exposed, imagewise, to light of such intensity that a latent image is formed in the outer layer without the formation of an appreciable image in the lower speed inner layer. The latent image in the outer layer is then developed in a silver halide developing solution containing iodide ion to form a silver image which modulates, imagewise, the diffusion of iodide ion, through the layer to form a secondary image in the inner layer in register with the primary image. The primary and secondary images may be formed simultaneously in the step during conventional development of the primary silver image but, where secondary image formation interferes with primary image formation, the images may be formed sequentially in separate steps. Where the primary image may have high fog, stain or other undesirable properties, it may be physically or chemically removed to reveal the secondary image in the underlayer.

In a particularly preferred embodiment of the invention, both the primary and secondary images are formed during a single development step to give a conventional negative silver image which is reinforced by the simultaneous imagewise fogging of the inner emulsion layer by the acton of iodide ion. The reinforcement of the original image is particularly striking because of the much greater covering power of the image formed in the slower, fine grain emulsion of the inner layer.

In other embodiments, the secondary image may form as a result of the diffusion and mordanting of an anionic dye, the action of other fogging agents on the silver halide, e.g., thiourea at high pH, the action of sulfur compounds which may convert silver halide to the sulfide or render the silver halide more insoluble in silver halide solvents, etc.

Other fogging agents which may replace the iodide ion during development are such compounds as 2- and 4-hydroxybenzylidenerhodanine. G. Schwarz, Phot. Korr. 74, 84–5 (1938), found that these latter compounds showed antifogging action with silver bromide and silver iodide emulsions in a metol-hydroquinone developer, where as they fog silver chloride emulsions in the same developer.

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

EXAMPLE I

A photographic element was prepared by coating an aqueous gelatin dispersion of silver chlorobromide (70 mole percent silver chloride and 30 mole percent silver bromide) on a gelatin-subbed vinylidene chloride copolymer coated, biaxially oriented, polyethylene terephthalate photographic film base as described in Example IV of Alles, U.S. Patent 2,779,684. The dispersion (a lithographic emulsion) had a fog density less than 1/10 its maximum net image density and an optical density less than 0.4, as characterized and defined above, contained gelatin hardening agents, had a fine grain, was unsensitized and undigested, and was applied to the film base to give a coating weight corresponding to 59 mg./dm.^{2} of silver. Over this layer, there was coated an unhardened, fully-sensitized, large-grain, gelatino-silver bromoiodide, X-ray emulsion of approximately 98.4 mole percent silver bromide and 1.6 mole percent silver iodide to give a coating weight corresponding to 30 mg./dm.^{2} of silver. Finally, a thin gelatin antiabrasion overcoating was applied.

Two strips of this film were exposed to blue light in a conventional manner through a square-root-of-two neutral density stepwedge, according to a procedure based on the American Standard Method for the Sensitometry of Medical X-Ray Films—PH 2.9—1956. An exposure time of 0.08 sec. and a lamp color temperature of 2700° K. were used. The strips were then developed under appropriate safelight conditions, for 3 minutes in a solution of the following composition:

SOLUTION A

Water	ml	800
Na_2SO_3 (anhyd.)	g	800
Hydroquinone	g	16
1-phenyl-4-methyl-3-pyrazolidone	g	1
Boric acid	g	5.5
KBr	g	2
Solution of 5-nitrobenzimidazole nitrate (10 g. per liter of ethanol solution)	ml	40
Solution of 1-phenyl-5-mercaptotetrazole (10 g. per liter of ethanol solution)	ml	10
NaOH	g	24
Resorcinol	g	16

Water to make 1000 ml..

This development was followed by treatment for ½ min. in an aqueous short stop solution containing 20 ml. glacial acetic acid and 100 ml. 3.0 M KBr per liter of solution. Next, the strips were bathed 1 minute in 0.05 M KI, after which room lights were turned on and the unhardened X-ray emulsion was washed off in hot water to reveal yellow silver iodide negative images in the underlayers. The strips were fixed for 1 minute in a conventional acid-hypo fixing bath (Photo Lab. Index, 1959, p. 5–26) which left the silver iodide image but removed other silver halides.

Apparently the developed negative silver image in the outer layer served as a "window" through which iodide ion (from the 0.05 M KI solution) could migrate to the inner layer to form a silver iodide image in register with the original silver images. Migration of the iodide ion was modulated imagewise by reaction with undeveloped silver halide in the outer layer to form a positive silver iodide image in said layer.

After washing and drying, one of the strips was bathed in a dilute aqueous sodium sulfide solution to tone it brown. The other strip was bathed in an aqueous solution of thionine to dye the image violet.

EXAMPLE II

Another strip of film, exposed and developed in Solution A, as described in Example 1, was washed in water at 68° F. for 1 min., and then bathed in 0.1 molar Na_2S solution (aqueous) for 1 minute at 68°F. After a 3 minute water wash at 68°F., the outer layer was removed by washing it off in water at about 110°F. A negative silver sulfide image was revealed in the inner layer. The silver halide in the non-image areas was removed by treatment in the acid-hypo fixing bath as in Example I after which the film strip was washed and dried.

Optical densities of the processed strip were read on a Western Electric RA–1100C Densitometer through a visual yellow filter at the various exposure levels (steps of the sensitometric exposure) to give the following densities:

Exp. Step No.—	Tot. opt. den.
7	.07
8	.08
9	.09
10	.15
11	.30
12	.44
13	.79
14	1.23
15	1.71
16	1.74
17	1.78
18	1.81
19	1.86
20	1.86

(Total optical density includes that attributable to base support density and fog density.)

Apparently, the silver image in the outer layer again served as a "window" through which an anion (sulfide) could migrate imagewise into the inner layer to form an image in register with the original silver image.

EXAMPLE III

A two layer film was prepared in which the inner layer was a hardened gelatino-silver chloride emulsion which had a fog density less than 1/10 its maximum net image density and an optical density less than 0.4, as characterized and defined above, and had not been sensitized. The outer layer was an unhardened, fully sensitized bromoiodide emulsion (iodide content 4 mole percent). The inner layer had a coating weight of 28 mg./dm.^{2} of silver and the outer layer had a coating weight of 43 mg./dm.^{2}. Two film samples were exposed as in Example I. One sample was developed in Solution B and the other in Solution C (defined below). Both samples were developed for 2 minutes at 68° F.

Solution	B	C
Water, ml	.08	800
Na_2SO_3 (anhyd.), gm	80	80
Hydroquinone, gm	16	16
1-phenyl-4-methyl-3-pyrazolidone, gm	1	1
Boric acid, gm	5.5	5.5
KBr, gm	2	2
1.25% by weight 5-nitrobenzimidazole in alcohol, ml	40	40
1.25% by weight 1-phenyl-5-mercaptotetrazole in alcohol, ml	10	10
NaOH, gm	24	24
0.5 M KI, ml	0	30
Water to make, ml	1,000	1,000

The film samples were then treated in the acid-hypo fixing solution of Example I, washed and dried.

The following total optical densities were measured using the densitometer described in Example II:

Exposure step	Optical density, sample developed using—	
	Solution B	Solution C
E3	.08	.22
E5	.10	.31
E7	.15	.35
E9	.26	.91
E11	.46	2.10
E13	.74	3.04
E15	.98	3.76
E17	1.15	3.78
E19	1.32	3.82
Base+fog	.07	.22

The second sample showed intensification because of the diffusion of iodide ions through the developing silver

image of the outer layer to cause imagewise fogging of the silver chloride underlayer and produce a silver image in register with that of the outer layer.

EXAMPLE IV

Two strips of a two-layer film were prepared and exposed as in Example III. They were then developed for 5 minutes in Solution B of Example III to which had been added 16 g. of resorcinol to prevent tanning of the gelatin. The strips were then washed in water for 1 minute.

One of the strips (labeled "No. 2") was treated for 2 minutes at 68° F. in Solution D (see below) and washed in water for 1 minute. This treatment in Solution D with subsequent washing in water was omitted in the processing of the strip labeled "No. 1."

SOLUTION D

Water	ml	800
NaOH	g	40
1.25% by weight 2-mercaptothiazoline in ethanol	ml	100

Water to make 1000 ml.

Both strips were then treated for 30 seconds in a 1% by weight aqueous solution of acetic acid. The outer emulsion layers were washed off in warm water and the strips were developed for 5 minutes at 68° F. in Solution B of Example III to which had been added 0.1 gram of thiourea.

The inner emulsion layer of film strip No. 1 was completely and uniformly fogged because of the presence of the thiourea in the final developing solution. The inner emulsion layer of film strip No. 2 had a positive image relative to the original negative image of the outer layer which was produced in the first developing solution (Solution C plus resorcinol). This positive image resulted from imagewise diffusion of the 2-mercaptothiazoline of Solution D through the developed sliver image of the outer emulsion layer, and its action in preventing fog by thiourea during the final development.

EXAMPLE V

A photographic element was prepared wherein the film support and inner (lithographic) emulsion layer were identical to those described in Example I. As an outer emulsion layer, however, there was coated an unhardened, fully-sensitized, fine-grain, gelatino-silver chloride emulsion to give a coating weight corresponding to 36 mg./dm.^{2} of silver.

Four strips of this film were exposed through a square-root-of-two neutral density stepwedge to a No. 2 photoflood lamp operating at 55 volts for ½ second at a distance of 2 feet. The strips were developed for 45 seconds at 68° F. in a bromide-free hydroquinone developer, *Solution E*, prepared by mixing equal parts of the following solutions:

First Solution

Water	ml	500
Hydroquinone	g	45
Na_2SO_3 (anhyd.)	g	30
Sulfuric acid (C.P.)	ml	4

Cold water to make 1 liter.

Second Solution

Water	ml	500
Na_2CO_3 (anhyd.)	g	30
K_2CO_3	g	90
Na_2SO_3 (anhyd.)	g	90

Cold water to make 1 liter.

After development, the strips were bathed for 30 seconds in an acid short stop solution (5% by weight acetic acid in water), washed for 2 minutes in water and dried. The four strips were then treated as follows in solutions at 68° F. except as otherwise indicated.

STRIP 1

Developed 1 minute in Solution E, shortstop 30 seconds in aqueous 5% by weight acetic acid, fixed 2 minutes in 12.8% by weight aqueous sodium thiosulfate, washed off outer emulsion layer, in warm water, washed in water 5 minutes at 68° F. and dried.

STRIP 2

Washed off outer emulsion layer in warm water, rinsed 30 seconds in 68° F. water, developed 1 minute in Solution E, treated for 30 seconds in 5% by weight aqueous acetic acid, fixed 2 minutes in 12.8% by weight aqueous sodium thiosulfate, washed 2 minutes and dried.

STRIP 3

Developed 1 minute in Solution E plus 4.15 g. KBr per liter of solution, treated for 30 seconds in 5% by weight aqueous acetic acid, fixed for 2 minutes in 12.8% by weight aqueous sodium thiosulfate, washed off outer emulsion layer in warm water, washed 5 minutes in water at 68° F. and dried.

STRIP 4

Washed off top emulsion layer in warm water, rinsed 30 seconds in 68° F. water, developed 1 minute in Solution E plus 4.15 g. KBr per liter of solution, treated for 30 seconds in 5% by weight aqueous acetic acid, fixed 2 minutes in 12.8% by weight aqueous sodium thiosulfate, washed 2 minutes and dried.

Optical densities of the processed strips were read as described in Example II to give the following densities.

Strip No.	E1	E2	E3	E4	E5	E6	E7	E8
1	.04	.05	.06	.08	.10	.11	.12	.13
2	.04	.05	.06	.06	.07	.09	.11	.13
3	.18	.40	.67	2.10	2.74	3.12	3.25	33.3
4	4.0+	4.0+	4.0+	4.0+	4.0+	4.0+	4.0+	4.0+

The above data show that development of a negative silver image in the upper or outer layer causes only a very weak negative image to form in the inner or lower hardened emulsion layer if development is carried out in a bromide-free developer (see Strips No. 1 and 2). Treatment of the lower layer in the same developer containing KBr shows that the KBr fogs the layer uniformly to a maximum density of 4.0+ (see Strip 4). If the second development with KBr is carried out with the upper layer intact and containing a negative silver image the silver image acts as a window to allow imagewise diffusion of bromide ion into the lower layer where it fogs the emulsion to give a negative image similar to the negative image in the top layer (see Strip #3).

Similar results were obtained in the previous experiment when the intermediate drying step was omitted.

EXAMPLE VI

Another film strip from the two-layer photographic element of Example V, exposed and developed for 45 sec. in Solution E as in Example V, was bathed with mild agitation for 60 seconds at 68° F. in an alkaline solution with 2-mercapto-4-phenylthiazole (pH=8.8) which was prepared by adding 40 ml. of aqueous potassium bicarbonate (22 g./100 ml.) to 10 ml. of an ethanol solution of 2-mercapto-4-phenylthiazole (1 g./100 ml.) and diluting the mixture with water to a total volume of 400 ml. The film was then rinsed in cold water for 5 seconds, bathed 15 seconds in 5% aqueous acetic acid, the top emulsion layer washed off in warm water and the remaining hardened emulsion layer fixed for 30 seconds at 68° F. in the conventional acid-hypo fixing solution described in Example I.

After fixing, a silver halide image remained which was proportional in density to the original negative silver image formed in the upper emulsion layer. This negative silver halide image may be toned, converted to a silver sulfide image, developed by color coupling, or simply

fogged and reduced to silver in a conventional developer.

Apparently the ionized anionic mercaptan migrated through the silver "window" in the outer layer to imagewise insolubilize the silver halide emulsion in the inner layer with respect to a silver halide solvent such as aqueous sodium thiosulfate.

EXAMPLE VII

An exposed film strip from the element prepared in Example I was developed in the following catechol developer (Solution F) for 2 minutes at 68° F., rinsed in 2% by weight aqueous acetic acid for 15 seconds at 68° F., washed 1 minute in water at 68° F., the top emulsion layer washed off in warm (110°–120° F.) water, fixed 3 minutes at 68° F. in the fixing solution of Example I, washed 5 minutes at 68° F., dried and the densities read as in Example II to give the results below.

SOLUTION F (CATECHOL DEVELOPER)

Water	ml	800
Na_2SO_3 (anhyd.)	g	100
Catechol	g	18
KI	g	2.5
NaOH	g	15

Water to make 1 liter.

Exp. Step No.	Density
8	.07
9	.09
10	.20
11	.41
12	.56
13	1.16
14	1.61
15	1.92
16	2.02
17	2.75
18	3.11
19	3.52
20	4.0+

EXAMPLE VIII

An exposed film strip from the element prepared in Example I was developed for 3 minutes at 68° F. in the following metol-hydroquinone developer:

SOLUTION G (METAL=HQ DEVELOPER)

Water	ml	800
Metol	g	3
Na_2SO_3 (anhyd.)	g	50
Hydroquinone	g	9
K_2CO_3	g	50
KBr	g	4.5

Water to make 1000 ml.

The strip was bathed for 15 seconds in 2% by weight aqueous acetic acid at 68° F., washed in water for 1 minute at 68° F., and developed 5 minutes at 68° F. in the aforementioned Solution G except that the hydroquinone was omitted and 2.5 g. KI added per liter. The strip was then treated for 15 seconds in 2% by weight aqueous acetic acid at 68° F., washed 1 minute in water at 68° F., the top emulsion layer washed off with hot water (110–120° F.), fixed 3 minutes at 68° F. in the acid-hypo fixing solution of Example I, dried and read as in Example II to give the following optical densities:

Exp. Step No.—	Density
1	.10
2	.10
3	.10
4	.10
5	.12
6	.15
7	.18
8	.23
9	.29
10	.41
11	.59
12	.80
13	.93
14	1.17
15	1.46
16	1.88
17	2.04
18	2.61
19	3.28
20	3.94
21	4.0+

EXAMPLE IX

A photographic element was prepared wherein the film support and inner (lithographic) and outer (X-ray) emulsion layers were identical to those described in Example I. A similar photographic element was prepared having only the inner (lithographic) emulsion layer but no outer (X-ray) emulsion layer. Film strips of these elements were given sensitometric exposures as described in Example I and processed in solutions at 68° F. as follows:

Test	Film element	Processing
1	Single layer element described above.	Developed 2′ in Solution A of Ex. I, treated 15 sec. in the acid short-stop solution of Ex. I, fixed 5′ in the fixing solution of Ex. I, washed in water, dried and the densities read as in Example II.
2	Two-layer element described above.	Developed 2′ in Solution A of Ex. 1, treated 15 sec. in acid short-stop solution as in Test 1, washed off outer emulsion layer in hot water, fixed 5′ in the fixing solution of Ex. I, washed, dried and read as in Test 1.
3	Same as in Test 2.	Repeated Test 2 but did not wash off outer emulsion layer.
4	Same as in Test 2.	Repeated Test 3 but added 0.4 g. KI per liter of Developer-Solution A of Ex. I.
5	Same as in Test 2.	Repeated Test 4 but washed off outer emulsion layer after the short-stop bath as in Test 2.
6	Single layer element described above.	Unexposed and processed as in Test 4.

The resulting densities and fog values are as follows:

Exposure	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
E1	0.00	0.00	0.05	0.17	0.01	
E2	0.00	0.00	0.05	0.17	0.01	
E3	0.00	0.00	0.05	0.17	0.01	
E4	0.00	0.00	0.05	0.18	0.01	
E5	0.00	0.00	0.05	0.20	0.01	
E6	0.00	0.00	0.05	0.24	0.01	
E7	0.00	0.00	0.05	0.28	0.01	
E8	0.00	0.00	0.07	0.33	0.01	
E9	0.00	0.00	0.10	0.42	0.01	
E10	0.00	0.00	0.12	0.63	0.02	
E11	0.00	0.00	0.21	0.90	0.12	
E12	0.00	0.00	0.31	1.17	0.31	
E13	0.00	0.00	0.38	1.65	0.59	
E14	0.00	0.00	0.40	2.00	0.75	
E15	0.00	0.00	0.56	2.36	0.80	
E16	0.00	0.00	0.63	2.42	0.85	
E17	0.00	0.00	0.67	2.50	0.90	
E18	0.00	0.00	0.67	2.65	0.96	
E19	0.00	0.00	0.70	3.10	1.29	
E20	0.00	0.00	0.71	4.00	1.68	
E21	0.00	0.00	0.71	4.00+	2.30	
FOG	0.01	0.00	0.05	0.17	0.01	4.00+

Conclusions

Tests 1 and 2 show that the lithographic emulsion has no fog and is unaffected by the image exposure. Test 6 shows that the addition of 0.4 g. KI/liter fogs the litho emulsion completely. Test 3 shows the amount of image and fog density developed in an X-ray emulsion in the absence of KI. Test 4 shows the effect on both litho and X-ray emulsion due to the addition of KI. Test 5 shows the imagewise fogging action of KI on the litho emulsion. The difference in image density between Tests 4 and 5 represents the amount of image density developed in the X-ray emulsion in the presence of KI.

The process of this invention is applicable to various types of photographic elements in which the contiguous silver halide emulsion layers may contain the same or

different types of silver halide crystals. The crystals may be silver salts of bromine or chlorine or of various mixtures of bromine, chlorine and iodine. The essential requirement is that the element be capable of having a latent image formed in the outer layer which is developable to a visible image without the formation of an appreciable image in the inner layer. The outer layer should, desirably, be more sensitive to light than the inner layer and the inner one should be unfogged, i.e., have a fog value of from 0 to 0.40. Other conditions such as grain size, sensitization, etc. being the same, an emulsion containing crystals of silver bromide or silver bromoiodide is more sensitive than one containing, e.g., silver chloride. However, it is possible to obtain the desired differential in light sensitivity in two emulsions having the same type of silver halide crystal, e.g., by sensitizing to a higher level the emulsion to be used for the outer coating. It is even possible to make a double-layer coating of the same emulsion, then treat the outer layer so as to give it the required additional light-sensitivity, e.g., by bathing in a chemical sensitizing solution. Also, the outer emulsion layer may be sensitized to radiation to which the inner layer does not respond, e.g., to light of the green or red portions of the visible spectrum.

While the invention has been described with respect to gelatin silver halide emulsions, various other water-permeable organic colloid binding agents for silver halide crystals can be used in place of all or a part of the gelatin. Suitable colloids include albumen, casein, alginic acid and the alginates; synthetic colloids, e.g., polyvinyl alcohol, polyvinyl acetals with o-sulfobenzaldehyde, etc.; the methacrylamide/acrylic acid copolymers of U.S. Patents 2,311,548, 2,592,107 and 2,611,763; the 1,2-dithiolanes of U.S. Patent 2,728,668, the copolymers of Shacklett U.S. Patent 2,777,872, dextran, dextrin and polyvinyl pyrrolidone.

The emulsions may be coated on any type of support such as paper or films, e.g., cellulose esters, e.g., cellulose acetate and cellulose acetate/butyrate; super-polymers, e.g., polyethylene terephthalates, polyethylene terephthalate/isophthalate or polyethylene terephthalate/phthalate, etc., which may have various anchor layers and/or sublayers. The film supports may be clear or transparent or tinted blue, etc. or may be opaque white by using an opacifying agent in or on the base. The coated element may contain auxiliary layers such as non-halation layers or antiabrasion layers.

The emulsions (particularly the outer emulsion) may contain any of the well-known optical sensitizing dyes as well as non-optical sensitizers containing labile sulfur, e.g., allyl isothiocyanate, allyl diethyl thiourea, phenyl isothiocyanate and sodium thiocyanate, the polyoxyalkylene ethers disclosed 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 nonoptical sensitizers such as amines as taught by Staud et al. U.S. Patent 1,925,508 and metal salts as taught by Baldsiefen U.S. Patent 2,540,085 and Baldsiefen et al. U.S. Patent 2,540,086 may also be used. Antifoggants, e.g. benzotriazole and triazaindenes can be used. The usual hardeners, i.e., chrome alum, formaldehyde, muchochloric acid, etc. are suitable for use in the inner emulsion but should not be used in the outer emulsion if it is desired to remove the outer emulsion layer, e.g., in order to remove an undesirable strain. Other emulsion adjuvants well known in the art may be added, e.g., matting agents, plasticizers, toners, color-formers, optical brightening agents, coating aids, image color modifiers, etc.

The process of the invention can be advantageously applied in a variety of photographic film elements including photographic films of positive or negative types, X-ray films, motion picture films, portrait films, photographic papers, etc.

An advantage of this invention resides in the fact that it increases the covering power of the photographic image without the loss of speed which normally accompanies an increase in covering power. Thus advantage may be taken of the very high covering power of a slow, fine grain emulsion (the inner layer) while the sensitivity to light is equal to that of the high speed, large grain, outer emulsion layer in which the original image is formed. The increased covering power may be used to give either (1) higher speed, contrast, and maximum density or (2) equivalent sensitometric characteristics with less silver halide coating weight (and, therefore, lower manufacturing costs). A further advantage is the relatively simple processing required, particularly in that preferred embodiment wherein the primary and secondary images are formed in a single development step. Yet another advantage is the versatility of the invention which permits the formation of a variety of different types of images. Still other advantages are apparent from the specific embodiments of the invention that are disclosed in Example VI wherein a silver halide (rather than silver) negative image is formed; this silver halide image provides flexibility for the process since the image can subsequently be toned, reduced to silver, sulfided, color coupled, etc. Still further advantages will be apparent from the above description of the invention.

I claim:

1. A process which comprises

(1) subjecting to an imagewise exposure and thereby forming a latent image in the outer unfogged light-sensitive silver halide emulsion layer of a photographic element having, on a support, a contiguous inner emulsion layer comprising unfogged internal silver halide grains and of such sensitivity that said imagewise exposure results in development of less than one-tenth of the available silver halide in the inner layer, said inner unfogged layer being one which at a coating weight of 540 mg./sq. foot of silver will produce an optical density of less than 0.4 in unexposed areas when developed for 5 minutes at 65° F. in the following developer:

	Grams
N-methyl-p-aminophenol sulfate	2.0
Sodium sulfite, desiccated	90.0
Hydroquinone	8.0
Sodium carbonate, monohydrate	52.5
Potassium bromide	5.0
Sodium thiosulfate	10.0
Water to 1 liter.	

the silver halides of both layers being in a water-permeable, macromolecular, organic colloid binding agent,

(2) treating said outer layer with an aqueous photographic developer solution to form a visible silver image in said layer, and

(3) not earlier than step (2) treating the outer layer of the element with an aqueous solution containing before the treating step an anion capable of forming a silver salt which is more insoluble in water than the silver halide of either of said emulsion layers, said anion diffusing imagewise differentially through the outer layer and forming in the inner layer a silver salt image from said anion in register with the earlier formed silver image in the outer layer.

2. A process according to claim **1** wherein the outer layer is a large-grain, high-speed silver halide emulsion layer.

3. A process according to claim **1** wherein the outer layer is a large-grain, high-speed silver bromoiodide emulsion layer and the inner layer is an undigested, unsensitized silver chlorobromide emulsion layer.

4. A process according to claim **1** wherein said anion is an iodide anion.

5. A process according to claim **1** wherein steps (2) and (3) are simultaneous by having the anion in an aqueous developer solution.

6. A process according to claim **1** wherein steps (2)

and (3) are simultaneous by having an iodide anion in the developer solution.

7. A process according to claim 1 wherein step (3) follows step (2).

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