

1

3,625,689

**HIGH-CONTRAST PHOTOGRAPHIC ELEMENTS
AND METHOD FOR PROCESSING SAME****Eugene D. Salesin and Thomas E. Whiteley, Rochester,
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ter, N.Y.****No Drawing. Filed Aug. 18, 1967, Ser. No. 661,530****Int. Cl. G03c 5/26****U.S. Cl. 96—50****14 Claims****ABSTRACT OF THE DISCLOSURE**

High-contrast photographic elements comprising a support coated with a silver halide emulsion which contains a dispersed polymerized vinyl compound and the halide comprises at least about 85 mole percent chloride, about 0.1 to about 5 mole percent iodide and the balance bromide, and method for processing same in a continuous transport processing machine wherein the developer contains a carbonyl bisulfite-amine condensation product.

BACKGROUND OF THE INVENTION**Field of the invention**

This invention relates to photographic materials, their preparation and use. One aspect of the invention relates to a continuous process for processing exposed high-contrast photographic elements in a continuous transport processing machine wherein certain developers must be employed in combination with certain silver halide emulsions as defined hereinafter in order to improve dot quality, increase effective contrast, reduce drag streaks and improve the shape of its H and D curve. Another aspect of the invention relates to the high-contrast, photographic elements themselves.

Description of the prior art

In the graphic arts field, where it is desired to make photographic line and halftone reproductions, it is customary to employ emulsions having extremely high contrast. In development, the developing areas grow autocatalytically at a very high developing rate to produce an extremely high contrast which is necessary for halftone patterns. Developers for use with extremely high-contrast photographic films are quite different in composition from typical black-and-white film developers. In order to obtain very high contrast and sharp halftone dots, it has been the practice to formulate developers for such films from essentially hydroquinone, an alkali, an alkali metal bromide and a low level of sulfite ion. The low level of sulfite ion partially stabilizes the developer solution for a short period of time and is achieved in all known commercial developers of this type by the use of sodium formaldehyde bisulfite, which acts as a sulfite ion buffer. These developer solutions must be stored in two parts, however, since the sodium formaldehyde bisulfite will dissociate at a high pH to give not only the desired sulfite ion but an equimolar amount of formaldehyde which will react with hydroquinone to destroy its developing power.

In reproducing continuous tone material, it is customary to make a halftone photographic intermediate, usually a film negative, in which the gradations in tone are represented by differing sizes of dots of uniform density. The shape, density and uniformity of the halftone dots

2

are closely correlated to the quality of the resulting picture.

The developer solutions for high-contrast films presently used in continuous transport processing machines also have a number of disadvantages. The photographic quality obtained with a given film is usually inferior to that obtained in careful tray processing. The sensitivity of high-contrast films to developer exhaustion products and variations in local developing agent concentration makes these films vulnerable to directional drag streaks in film halftone areas under conditions of machine processing. These drag streaks occur in areas of high development (50–90% dots) which are adjacent to areas of low development (dot area of 20% or less). The drag streaks are formed by more development occurring because the developer which is "dragged in" from the area of low development contains more developing agent and less exhaustion products (primarily bromide ion) than the developer that would normally be in that area. The dots in a high-contrast film are also distorted and exhibit size changes depending on the orientation and direction of travel through the machine processor. This dot distortion is manifested by discontinuities or plateaus in the H and D curve of high-contrast films which are processed in continuous transport processing machines. The elimination or reduction of drag streaks and dot distortions would be a considerable advance in the art.

SUMMARY OF THE INVENTION

In my invention, there is provided high-contrast photographic elements comprising a support coated with a silver halide emulsion, said silver halide emulsion containing a dispersed polymerized vinyl compound, and said halide comprising at least about 85 mole percent chloride, about 0.1 to about 5 mole percent iodide and the balance bromide. I also provide a continuous process for processing such elements after exposure wherein said element is processed in one continuous motion by transporting it into, through and out of at least one processing solution in the manner shown, for example, by U.S. Patents 3,025,779 of Russell and Kunz issued Mar. 20, 1962; 3,078,024 of Sardeson issued Feb. 19, 1963; 3,122,086 of Fitch issued Feb. 25, 1964; 3,149,551 of Cramer issued Sept. 22, 1964; 3,156,173 of Meyer issued Nov. 10, 1964; and 3,224,356 of Fleisher and Hixon issued Feb. 21, 1965; and wherein said element is developed in a liquid developer composition comprising a developing agent and a carbonyl bisulfite-amine condensation product.

**DESCRIPTION OF THE PREFERRED
EMBODIMENTS**

The developing agents which can be employed in the instant invention can be any of those suitable for the intended purpose. Useful silver halide developing agents, for example, include the dihydroxybenzenes such as hydroquinone; chlorohydroquinone; bromohydroquinone; isopropylhydroquinone; toluhydroquinone; methylhydroquinone; 2,3-dichlorohydroquinone; 2,5-dimethylhydroquinone; 2,3-dibromohydroquinone; 1,4-dihydroxy-2-acetophenone - 2,5 - dimethylhydroquinone; 2,5-diethylhydroquinone; 2,5-di - p - phenethylhydroquinone; 2,5-dibenzoylaminoquinone; 2,5 - diacetaminohydroquinone; etc. Esters of such compounds, e.g., formates and acetates, can also be employed. These developing agents can be used alone or in any combination and can be employed in any concentration which is effective for de-

velopment. A suitable concentration for the developing agent is from about 0.05 to about 0.50 mole per liter of developer composition and is preferably from about 0.10 to about 0.30 mole per liter of developer composition.

The carbonyl bisulfite-amine condensation products which can be used in the developer composition employed in my invention are preferably formaldehyde bisulfite-amine condensation products such as

sodium-2-hydroxyethylaminomethane sulfonate;
sodium-2-hydroxypropylaminomethane sulfonate;
sodium-1,1-dimethyl-2-hydroxyethylaminomethane sulfonate;
sodium-1,1-bis(hydroxymethyl)ethylaminomethane sulfonate;
sodium-tris(hydroxymethyl)methylaminomethane sulfonate;
sodium-3-hydroxypropylaminomethane sulfonate;
sodium-bis(2-hydroxyethyl)aminomethane sulfonate;
sodium-N,N-bis[2-(1-hydroxy)propyl]aminomethane sulfonate;
sodium-N-isopropyl-N-(2-hydroxyethyl)-aminomethane sulfonate;
sodium-N-ethyl-N-(2-hydroxyethyl)aminomethane sulfonate; and
sodium-N-methyl-N-(2-hydroxyethyl)-aminomethane sulfonate.

The carbonyl bisulfite-amine condensation products can be used alone or in any combination and can be employed in any concentration which is effective to provide a low level of sulfite ion for the developer composition. A suitable concentration for the carbonyl bisulfite-amine condensation product is from about 0.1 to about 1.0 mole per liter of liquid developer composition and is preferably from about 0.25 to about 0.50 mole per liter of liquid developer composition.

The carbonyl bisulfite-amine condensation product can be added to the developer composition as a separate compound or formed in situ. Methods for preparing these compounds are disclosed, for example, in U.S. Pat. 2,388,816 of Bean issued Nov. 13, 1945. In this specification and claims, it is meant to include within the definition of carbonyl bisulfiteamine condensation product either the compound itself or the individual components which form the compound in situ.

The high-contrast photographic elements of the instant invention comprise a support coated with a silver halide emulsion layer in which the halide comprises at least about 85 mole percent chloride, about 0.1 to about 5 mole percent iodide and the balance bromide. Preferably, the halide in said silver halide emulsion comprises at least about 90 mole percent chloride, about 0.5 to about 2 mole percent iodide and the balance bromide, since such preferred emulsions provide particularly good results in eliminating drag streaks and dot distortions.

The silver halide emulsion layer of the high-contrast photographic elements of the instant invention can contain any of the hydrophilic water-permeable binding materials suitable for this purpose in combination with a dispersed polymerized vinyl compound. Suitable binding materials include, for example, gelatin, colloidal albumin, cellulose derivatives, etc. Mixtures of these binding agents can also be employed. The vinyl compound in the silver halide emulsion must be a dispersed polymerized vinyl compound, e.g., a polymeric latex or hydrosol. Such vinyl compounds are to be distinguished from water-soluble polymerized vinyl compounds which will not function in the same manner in my invention. Dispersed polymerized vinyl compounds are disclosed, for example, in U.S. Pats. 3,142,568 of Nottorf issued July 28, 1964; 3,193,386 of White issued July 6, 1965; 3,062,674 of Houck, Smith and Yudelson issued Nov. 6, 1962; and 3,220,844 of Houck, Smith and Yudelson issued Nov. 30, 1965; and include the water-insoluble polymers of

alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, interpolymers of alkyl acrylates with acrylic acids, acryloyloxy alkyl sulfonic acids, acetoacetoxyalkyl acrylates such as 2-acetoacetoxyethyl methacrylate, and the like. These vinyl polymers are generally employed in concentrations in the range of about 20 to about 80 percent, preferably at least 50 percent, by weight, based on the weight of the binding agent. Further details concerning these polymers can be found in co-pending application Ser. No. 454,683 of Dykstra filed May 10, 1965, now Pat. No. 3,411,911, and application Ser. No. 625,593 of Smith filed Mar. 24, 1967 now Pat. No. 3,488,708.

The silver halide emulsion of the high-contrast photographic elements of the instant invention can be coated on a wide variety of supports. Hydrophilic colloid layers can be coated on one or both sides of the support, if desired. Typical supports are cellulose nitrate film, cellulose ester film, polyvinyl acetal film, polystyrene film, poly(ethylene terephthalate) film, and related films or resinous materials, as well as glass, paper, metal and the like. Supports such as paper, which are coated with α -olefin polymers, particularly polymers of α -olefins containing two or more carbon atoms, as exemplified by polyethylene, polypropylene, ethylene-butene copolymers and the like can also be employed.

The silver halide emulsions of the high-contrast photographic elements of the instant invention can be sensitized using any of the well-known techniques in emulsion making, for example, by digesting with naturally active gelatin or various sulfur, selenium, tellurium compounds and/or gold compounds. The emulsions can be sensitized with salts of noble metals of Group VIII of the Periodic Table which have an atomic weight greater than 100. The emulsions can also contain addenda which increase speed and/or contrast such as quaternary ammonium salts, ployethylene glycols, thioether sensitizers or combinations thereof.

The silver halide emulsion of the high-contrast photographic elements of the instant invention can conveniently be ortho-sensitized or pan-sensitized with spectral sensitizing dyes. For instance, these emulsions can be spectrally sensitized by treating with a solution of a sensitizing dye in an organic solvent. Sensitizing dyes useful in sensitizing such emulsions are described, for example, in U.S. Patents 2,526,632 of Brooker and White issued Oct. 24, 1950, and 2,503,776 of Sprague issued Apr. 11, 1950. Spectral sensitizers which can be used are the cyanines, merocyanines, complex (trinuclear) cyanines, complex (trinuclear) merocyanines, styryls, and hemicyanines.

The silver halide emulsion of the high contrast photographic elements of the instant invention can also contain conventional addenda such as gelatin plasticizers, coating aids, antifoggants such as the azaindines and hardeners such as aldehyde hardeners, e.g., formaldehyde, mucochloric acid, glutaraldehyde bis(sodium bisulfite), maleic dialdehyde, aziridines, dioxane derivatives and oxypoly-saccharides.

Other methods for reducing or eliminating drag streaks and dot distortions in continuous transport processing machines are found in application Ser. No. 661,532 of my co-worker Masseth filed concurrently herewith and entitled "Photographic Developer Composition and Process of Using Same"; application Ser. No. 661,531 of my co-worker Milton filed concurrently herewith and entitled "High-Contrast Photographic Elements and Method for Processing Same"; and application Ser. No. 661,533 of my co-worker Milton filed concurrently herewith and entitled "Method for Processing High-Contrast Photographic Elements."

This invention can be further illustrated by the following examples of preferred embodiments thereof although it will be understood that these examples are included merely for purposes of illustration and are not intended

5

to limit the scope of the invention unless otherwise specifically indicated.

EXAMPLE 1

Effect of dispersed polymerized vinyl compound

(A) A fine-grain silver chlorobromiodide gelatin emulsion containing 90 mole percent chloride, 9 mole percent bromide and 1 mole percent iodide is chemically sensitized with sulfur and gold compounds and coated on a polyethylene terephthalate support at a coverage of 456 milligrams of silver per square foot and 452 milligrams of gelatin per square foot. A gelatin overcoat is coated over the emulsion layer at a coverage of 82.6 milligrams per square foot.

(B) A coated element similar to (A) is prepared but with 296 milligrams per square foot of copoly(methyl acrylate-sulfopropyl acrylate) and 296 milligrams of gelatin per square foot in the emulsion layer.

(C) A coated element similar to (A) is prepared but with 296 milligrams per square foot of copoly(methyl acrylate-sulfopropyl acrylate-2-acetoacetoxyethyl methacrylate) and 296 milligrams of gelatin per square foot in the emulsion layer.

The coated elements are then exposed, using tungsten illumination, to a step wedge through a magenta contact screen. The elements are then processed in a Kodak Roller Transport 324 Film Processor, of the type shown in U.S. Pat. 3,025,779 of Russell and Kunz, issued Mar. 20, 1962, employing the following developer which is disclosed and claimed in my co-worker Masseth's co-pending application Ser. No. 661,532 filed concurrently herewith and entitled "Photographic Developer Composition and Process of Using Same":

	Grams
Sodium-bis-(2-hydroxyethyl) - aminomethane sulfonate ¹	82.0
Sodium sulfite	30.0
Boric acid	7.5
Hydroquinone	22.5
Potassium bromide	1.6
2,2'-iminodiethanol	39.0
Water to make 1 liter.	
pH	9.5

¹ Sodium formaldehyde bisulfite and 2,2'-iminodiethanol can be used to form this compound in situ.

The coated elements are processed using the various development times listed below with the following results:

Coated element	Relative speed change				Effective contrast ¹				Drag streaks	Curve shape
	1½' dev.	1¾' dev.	2' dev.	2¼' dev.	1½' dev.	1¾' dev.	2' dev.	2¼' dev.		
A (control)	100	+114	+176	+317	0.8	2.4	3.1	2.95	Severe.....	Poor.
B	550	+18	+35	+61	8.0	8.2	9.2	8.5	Moderate.....	Good.
C	468	+26	+48	+66	7.0	8.6	9.5	9.5	Do.....	Do.

¹ Slope of the straight line between two points which are 0.3 Log E apart on the D vs. Log E curve, where the lower point has a density of 0.1 above fog.

The above results indicates that the time-development H and D curves of coated elements (B) and (C) are closer together and their spacing more uniform than the control as evidenced by the relative speed change. Coated elements (B) and (C) also have a greatly improved effective contrast than the control, drag streaks are reduced and the poor curve shape of the control is eliminated.

EXAMPLE 2

Effect of iodide content

(A) A silver chlorobromide gelatin emulsion containing 90 mole percent chloride and 10 mole percent bromide is chemically sensitized with sulfur and gold compounds and coated on a polyethylene terephthalate support at a coverage of 470 milligrams of silver per square foot, 300 milligrams of gelatin per square foot and 300 milligrams of a methylacrylate-sulfopropyl acrylate latex per square foot. A gelatin overcoat is coated over the emulsion layer at a coverage of 80 milligrams per square foot.

6

(B) A coated element similar to (A) is prepared but with the emulsion containing 90 mole percent chloride, 9 mole percent bromide and 1 mole percent iodide.

The coated elements are then exposed on an intensity scale sensitometer and then processed in a Kodak Roller Transport 324 Film processor employing the following developer:

	Grams
Sodium-β-hydroxyethylaminomethane sulfonate ..	322
Hydroquinone bromide	90
Potassium bromide	6.3
Water to make 1 liter.	
pH	10.0 ¹

¹ pH adjusted with sodium carbonate.

The following results are obtained at a development time of 2 minutes:

Coated element	Effective contrast	Curve shape
A (control—no iodide)	0.185	Very poor.
B (contains iodide)	3.6	Good.

It can be seen from the above results that by introducing iodide into the silver halide crystal, a considerable improvement is obtained in both effective contrast and curve shape when such elements contain a polymerized vinyl compound in the emulsion and when such elements are processed in a continuous transport processing machine employing a developer which contains a carbonyl bisulfite-amine condensation product. This result is very surprising in view of prior art teachings that iodide in the crystal is not desirable in lith-type emulsions. See, for example, U.S. Pat. 3,178,289 of Sottysiak issued Apr. 13, 1965, column 1, lines 69-71, and column 2, lines 1-3:

"These emulsions should be free of iodide, although small concentrations of iodide can be tolerated so long as they do not exceed 0.5 percent of iodide based on the amount of silver nitrate used in the preparation of the silver halide emulsions."

EXAMPLE 3

(A) A fine-grain silver chlorobromiodide gelatin emul-

sion containing 90 mole percent chloride, 9 mole percent bromide and 1 mole percent iodide is chemically sensitized as in Example 1 and coated on a polyethylene terephthalate support at a coverage of 456 milligrams of silver per square foot, 296 milligrams of gelatin per square foot and 296 milligrams of copoly(methyl acrylate-sulfopropyl acrylate-2-acetoacetoxyethyl methacrylate) per square foot. A gelatin overcoat is coated over the emulsion layer at a coverage of 83 milligrams per square foot.

(B) A coated element similar to (A) is prepared but with 80 mole percent chloride, 19 mole percent bromide and 1 mole percent iodide.

(C) A coated element similar to (A) is prepared but with 70 mole percent chloride, 29 mole percent bromide and 1 mole percent iodide.

(D) A coated element similar to (A) is prepared but with 40 mole percent chloride, 59 mole percent bromide and 1 mole percent iodide.

7

The coated elements are then exposed and processed as in Example 1 employing a 1 $\frac{3}{4}$ minute development time with the following results:

Coated element:	Mole percent Cl/Br/I	Relative speed	Contrast	Dot ¹ quality
A-----	90:9:1	100	6.5	8
B-----	80:19:1	40	3.7	7
C-----	70:29:1	25	3.5	6
D-----	40:59:1	24	5.5	4

¹ Determined by examining the dot areas and assigning a number ranging from 9 (excellent) to 1 (extremely poor).

It can be seen from the above results that high-contrast photographic elements wherein the silver halide emulsion contains a dispersed polymerized vinyl compound and wherein the halide comprises at least 85 mole percent chloride, 0.1 to 5 mole percent iodide and the balance bromide, provides significant increases in relative speed, contrast and dot quality.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention as described hereinbefore and as defined in the appended claims.

I claim:

1. In a continuous process for processing an exposed, high-contrast photographic element comprising a support coated with a silver halide emulsion wherein said element is processed in one continuous motion by transporting it into, through and out of at least one processing solution, the improvement comprising:

(a) developing said element in a liquid developer composition comprising a developing agent and a carbonyl bisulfite-amine condensation product,

(b) said silver halide containing a dispersed water-insoluble polymer of an alkyl acrylate, methacrylate, sulfoalkyl acrylate, sulfoalkylmethacrylate or acrylic acid, and

(c) said halide comprising at least about 85 mole percent chloride, about 0.1 to about 5 mole percent iodide and the balance bromide.

2. The process of claim 1 wherein said developing agent is a dihydroxybenzene developing agent and said carbonyl bisulfite-amine condensation product is a formaldehyde-bisulfite-amine condensation product.

3. The process of claim 2 wherein said dihydroxybenzene developing agent is present in a concentration of from about 0.05 to about 0.50 mole per liter of developer composition and said formaldehyde bisulfite-amine condensation product is present in a concentration of from

8

about 0.10 to about 1.0 mole per liter of developer composition.

4. The process of claim 3 wherein said dihydroxybenzene developing agent is hydroquinone.

5. The process of claim 4 wherein said formaldehyde bisulfite-amine condensation product is sodium-bis(2-hydroxyethyl)aminoethane sulfonate.

6. The process of claim 3 wherein said photographic element is transported by rollers.

7. The process of claim 2 wherein said vinyl compound is a water-insoluble polymer of an alkyl acrylate or alkyl methacrylate.

8. The process of claim 5 wherein said dispersed water-insoluble polymer is a polymer of an alkyl acrylate or an alkyl methacrylate.

9. The process of claim 2 wherein said halide comprises about 90 mole percent chloride, about 1 mole percent iodide and about 9 mole percent bromide.

10. The process of claim 5 wherein said halide comprises about 90 mole percent chloride, about 1 mole percent iodide and about 9 mole percent bromide.

11. A high-contrast, photographic element comprising a support coated with a silver halide emulsion, said silver halide emulsion containing a dispersed water-insoluble polymer of an alkyl acrylate, methacrylate, sulfoalkyl acrylate, sulfoalkylmethacrylate or acrylic acid, and said halide comprising at least about 85 mole percent chloride, about 0.1 to about 5 mole percent iodide and the balance bromide.

12. The photographic element of claim 11 wherein said dispersed water-insoluble polymer is a polymer of an alkyl acrylate or alkyl methacrylate.

13. The photographic element of claim 12 wherein said halide comprises about 90 mole percent chloride, about 1 mole percent iodide and about 9 mole percent bromide.

14. The photographic element of claim 11 wherein said dispersed water-insoluble polymer is present in an amount ranging from about 20 to about 80 percent by weight based on the weight of total binding agent in said silver halide emulsion.

References Cited

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