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3,477,852

DIRECT-POSITIVE SILVER HALIDE EMULSION RESISTANT TO KINK-MARKING DESENSITIZATION

Norman Allentoff and Henry Harrison Fogler, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

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17 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to direct-positive photographic emulsions comprising fogged silver halide grains and processes for making the same wherein at least about 10 mole percent of said halide is chloride, less than about 5 mole percent of said halide is iodide and about 0.025 to about 0.5 mole of silver bromide, per mole of silver in said grains, forms a surface on said grains. In one aspect, direct-positive emulsions comprising fogged silver halide grains according to this invention provide a means for reducing desensitization due to kink-marking while improving sensitivity and maximum density upon image-wise exposure and chemical development.

This invention relates to photographic emulsions, their preparation and use. In one of its aspects, this invention relates to improved direct-positive photographic silver halide emulsions and photographic elements containing such emulsions. In another aspect, this invention relates to a means for reducing desensitization due to kink-marking while improving sensitivity and maximum density of direct-positive photographic emulsions and elements.

The use of fogged direct-positive photographic silver halide emulsions in the photographic field to obtain positive images is well known. However, when photographic elements containing fogged direct-positive photographic silver halide emulsion layers are physically deformed during handling, for example, by bending, latent image is removed from the silver halide in the grains present in the physically deformed areas. This causes a loss in maximum density (D_{max}) upon development and is known as kink-mark desensitization. This is obviously undesirable, particularly in photographic emulsions used in graphic arts applications where such materials must meet very high standards. Anti-kink agents have been added to photographic emulsions to inhibit kink-marking. However, such materials often reduce D_{max} and/or photographic speed, i.e., the sensitivity of an emulsion, to which they are added.

It is, of course, desirable to obtain photographic emulsions and elements, particularly direct-positive photographic emulsions and elements, which exhibit improved anti-kink as well as increased D_{max} and photographic speed or sensitivity. It is evident that a means for reducing susceptibility of fogged, direct-positive photographic silver halide emulsions and elements to kink-mark desensitization while also increasing D_{max} and photographic speed, would greatly enhance the art.

Accordingly, it is an object of this invention to provide photographic silver halide emulsions and elements exhibiting improved properties.

Another object of this invention is to provide fogged, direct-positive photographic silver halide emulsions and elements which combine resistance to kink, improved D_{max} and photographic speed.

Another object of this invention is to provide direct-positive photographic silver halide emulsions comprising fogged silver halide grains having a unique structure.

Still another object of this invention is to provide a

means for preparing fogged silver halide grains having surfaces of silver bromide.

Other objects and advantages of this invention will become apparent from an examination of the specification and claims which follow.

In accordance with this invention, it has been found that the above and other objects can be obtained with direct-positive photographic emulsions and elements comprising fogged silver halide grains in which chloride ions have been replaced by bromide ions to form at least a part of the surface of such grains.

One embodiment of this invention relates to a direct-positive photographic emulsion comprising fogged silver halide grains in which at least about 60 mole percent of said halide is bromide, at least about 10 mole percent of said halide is chloride and less than about 5 mole percent of said halide is iodide, about 0.025 to about 0.5 mole of bromide, per mole of silver, forming a surface on said grains.

Another embodiment of this invention relates to a photographic element comprising a support and at least one direct-positive photographic emulsion layer comprising fogged silver halide grains in which at least about 60 mole percent of said halide is bromide, at least about 10 mole percent of said halide is chloride and less than about 5 mole percent of said halide is iodide, about 0.025 to about 0.5 mole of bromide, per mole of silver, forming a surface on said grains.

Another embodiment of this invention relates to a method which comprises (1) reacting (a) photographic silver halide grains in which more than about 10 mole percent of said halide is chloride and less than about 5 mole percent of said halide is iodide with (b) a water soluble bromide salt to replace chloride on the surface of said grains, (2) stopping said reaction when the concentration of bromide in said grains is at least 60 mole percent and the concentration of chloride in said grains is no less than about 10 mole percent and (3) fogging said grains. Unless otherwise specifically indicated in the specification and/or claims, it is to be understood that the fogging step, identified as (3), can take place at any time prior to the use of the direct-positive emulsion, i.e., it can take place before, during or after the replacement of chloride ions by bromide ions on the grain surfaces.

Still another embodiment of this invention relates to a method which comprises (1) reacting (a) fogged photographic silver halide grains in which more than about 10 mole percent of said halide is chloride, at least about 40 mole percent of said halide is bromide, and less than about 5 mole percent of said halide is iodide with (b) a water soluble bromide salt to replace at least about 0.015 mole of chloride, per mole of silver, on the surface of said grains and (2) stopping said reaction when the concentration of said chloride in said grains is no less than about 10 mole percent.

It is a significant feature of this invention that the silver halide grains employed in the direct-positive photographic emulsions described herein contain at least about 10 mole percent chloride. Thus, a reduction in chloride content of the grains below about 10 mole percent has a significant deleterious effect on D_{max} of the photographic emulsion, as shown by Example 1 which follows. Similarly, as shown by Example 1, an iodide content in the silver halide grains above about 5 mole percent results in an undesirable increase in minimum density (D_{min}). Furthermore, as shown by Example 3, the fogged silver halide grains employed in the practice of this invention require a bromide content of at least 60 mole percent in order to exhibit the desired combination of physical and photographic properties.

The photographic silver halides employed in the practice of this invention are those in which bromide ions

form at least a part of the surface of the grains. Such grains comprise about 0.025 to about 0.5, preferably about 0.05 to about 0.3, mole of bromide, per mole of silver, on the surface of the grains. Silver halide grains of this type can be prepared by any method suitable for this purpose. One such suitable method is disclosed in McWilliams U.S. Patent 2,756,148, issued July 24, 1956, particularly as described in column 2, lines 4-8. A convenient method for preparing suitable silver halide grains comprises first forming silver chloride grains or crystals, for example silver chloride or silver chlorobromide crystals in an aqueous solution of a hydrophilic colloid, preferably gelatin and then adding, per mole of silver, about 0.025 to about 0.5, preferably about 0.05 to about 0.3 mole of a water soluble bromide salt to the solution. The chloride ions present on the surface of the photographic silver halide grains are replaced by the bromide ions from the more insoluble bromide salt. Suitable water soluble bromide salts which can be employed in this reaction include alkali metal salts such as sodium bromide or potassium bromide. Reaction temperatures are generally in the range of about 80° F. to about 200° F., preferably in the range of about 95° F. to about 180° F., although lower or higher temperatures can be used. The reaction is not particularly pressure dependent and, therefore, superatmospheric, atmospheric or subatmospheric pressures can be employed.

The photographic silver halide grains employed in the direct-positive emulsions and elements of this invention contain no less than about 10 mole percent chloride, at least about 60 mole percent bromide and less than about 5 mole percent iodide. A preferred class of photographic silver halides are those in which the halide is at least 10 mole percent chloride and more preferably about 20 mole percent chloride, at least about 60 mole percent bromide, and more preferably about 70 or 80 mole percent bromide, with less than about 1 percent of the halide being iodide. In preparing such grains, the photographic silver halide grains employed as the starting materials must, of course, contain more than about 10 mole percent of the chloride and no more than about 5 mole percent iodide. Suitable halides include, for example, silver chloride, silver chlorobromide, silver chlorobromiodide and the like.

The photographic silver halide grains employed in practicing this invention can be fogged using any method suitable for this purpose. The silver halide grains can be fogged before, during or after the formation of the silver bromide surface, but it is preferable to fog the emulsion prior to the addition of the water soluble bromide salt which forms the silver bromide surface by substitution of chloride ions. Where a silver bromide surface is formed on previously fogged silver halide grains, the halide in such previously fogged grains preferably comprises more than about 10 mole percent chloride, at least about 40 mole percent bromide and less than about 5 mole percent iodide. Sufficient water soluble bromide salt is added to replace at least about 0.015 mole, and preferably about 0.03 to about 0.2 mole of chloride, per mole of silver, on the surface of such previously fogged grains. The reaction is stopped when the concentration of chloride in the grains is no less than about 10 mole percent.

A suitable fogging procedure which can be used in the practice of this invention includes exposing the emulsion to light as disclosed in Shirk U.S. Patent 2,944,987 issued July 12, 1960. Other methods such as chemical fogging methods can also be used, e.g., fogging can be effected by chemical sensitization to fog using chemical sensitizing agents such as gold or noble metal sensitizers, sulfur sensitizers, such as labile sulfur compounds and the like. The silver halide grains can also be fogged by treating with reduction fogging agents, such as formaldehyde, stannous chloride, thiourea dioxide, such as those described in Hill U.S. Patent 3,062,651, issued Nov. 6, 1962. The silver halide grains can be fogged with a combina-

tion of fogging agents, e.g., the silver halide grains can be fogged by the addition of a reduction fogging agent in combination with a gold fogging agent. The fogging is generally sufficient to give a density of at least 2.0 when the coated emulsion is processed in a photographic developer.

Various colloids can be used as vehicles or binding agents in the direct-positive photographic materials of this invention. Satisfactory colloids which can be used for this purpose include any of the hydrophilic colloids generally employed in the photographic field, including, for example gelatin, colloidal albumin, polysaccharides, cellulose derivatives, synthetic resins such as polyvinyl compounds, including polyvinyl alcohol derivatives, acrylamide polymers and the like. In addition to the hydrophilic colloids, the vehicle or binding agent can contain hydrophobic colloids such as dispersed polymerized vinyl compounds, particularly those which increase the dimensional stability of photographic materials. Suitable compounds of this type include water-insoluble polymers of alkyl acrylates or methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

The photographic compositions described herein can be coated on a wide variety of supports in preparing the photographic elements. The photographic silver halide emulsions can be coated on one or both sides of the support, which is preferably transparent and/or flexible. Typical supports are cellulose nitrate film, cellulose ester film, polyvinyl acetal film, polystyrene film, polyethylene terephthalate film and other polyester film as well as glass, paper, metal, wood 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 give good results.

The photographic silver halide emulsion and other layers present in the photographic elements made according to this invention can be hardened with any suitable hardener including aldehyde hardeners such as formaldehyde and mucochloric acid, aziridine hardeners, hardeners which are derivatives of dioxane, oxy polysaccharides such as oxy starch, oxy plant gums and the like.

The photographic silver halide emulsion layers can contain additional additives, particularly those known to be beneficial in photographic emulsions including, for example, lubricating materials, stabilizers, speed increasing materials, absorbing dyes, plasticizers and the like. These photographic emulsions can also contain spectral sensitizing dyes. Suitable spectral sensitizers include the cyanines, merocyanines, complex(trinuclear)cyanines, complex(trinuclear)merocyanines, styryls and hemicyanines. Furthermore, these emulsions can contain color forming couplers or can be developed in solutions containing couplers or other color generating materials. The color forming couplers can be incorporated into the direct-positive photographic silver halide emulsion using any suitable technique, for example techniques of the type shown in Jelley et al. U.S. Patent 2,322,027, issued June 15, 1943, Fierke et al. U.S. Patent 2,801,171, issued July 30, 1957, Fisher U.S. Patents 1,055,155 and 1,102,028, issued Mar. 4, 1913 and June 30, 1914 respectively, and Wilmanns U.S. Patent 2,186,849, issued Jan. 9, 1940. They can also be developed using incorporated developers such as polyhydroxybenzenes, aminophenols, 3-pyrazolidones and the like. If desired, the photographic emulsions disclosed herein can be unhardened and can contain incorporated tanning developers such as those in which the tanning developing agent is hydroquinone or catechol. The direct positive photographic emulsions of this invention can also contain electron acceptors or desensitizers, particularly those which enhance solarization or the Herschel effect, as exemplified by the nitroheterocyclic compounds described in Kendall and Hill U.S. Patent 2,541,472 and the nitrostyrylcycloammonium quaternary salts and bases such as those described in Kendall et al. U.S. Patent 2,669,515.

It is sometimes advantageous to employ surface active agents or compatible mixtures of such agents in the preparation of the photographic materials described herein. Suitable agents of this type include non-ionic, ionic and amphoteric types, as exemplified by polyoxyalkylene derivatives, amphoteric amino acid dispersing agents, including sulfobetaines and the like. Such surface active agents are described in U.S. Patent 2,600,831, issued June 17, 1952, U.S. Patent 2,271,622, issued Feb. 3, 1942, U.S. Patent 2,271,623, issued Feb. 3, 1942, U.S. Patent 2,275,727, issued Mar. 10, 1942, U.S. Patent 2,787,604, issued Apr. 2, 1947, U.S. Patent 2,816,920, issued Dec. 17, 1947, U.S. Patent 2,739,891, issued Mar. 21, 1956 and Belgian Patent 652,862.

The loss in maximum density (D_{max}) of fogged, direct-positive silver halide emulsion layers due to physical deformation can be conveniently demonstrated by compressing a sample of film containing such a layer between two planes, one of which has a raised triangle and the other of which has a triangle of about three times the area of the first cut in it. The raised triangle is an isosceles triangle, the longer sides being about $\frac{9}{16}$ inch in length, the shorter side being about $\frac{7}{16}$ inch in length. The off-set of the raised triangle is about $\frac{1}{16}$ inch and the proportions of the depressed triangle are the same as those of the raised triangle. For testing purposes, a three kilogram weight is applied to the top of the raised triangle. The loss in D_{max} after development of the coating, fixing and washing in the usual manner can be rated on the basis of 0 for no loss in maximum density, 1 for very slight loss, 2 for slight loss, 3 for moderate loss and 4 for severe loss. These results are determined by comparison between the density of the unaffected and deformed portions of the film or by making actual density measurements with suitable equipment.

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

sensitometer. All the samples are processed for 2 minutes in Kodak D-11 developer, fixed, washed and dried. The loss in D_{max} due to kinking, determined as described hereinabove, is reported in the following Table 1. Photographic properties are also reported.

TABLE 1

	G. of KBr added per mole silver	Relative Speed	Gamma	D_{max}	D_{min}	D_{max} Loss
Coating:						
1.....	None	100	4.4	4.30	.17	4
2.....	4.5	224	4.9	4.40	.05	1
3.....	9.0	269	4.7	4.26	.04	0
4.....	13.5	417	3.3	4.31	.04	0

It can be seen from the above table that considerable improvement in sensitivity and in resistance to physical stress is obtained in the emulsions to which the soluble bromide has been added to form a silver bromide surface on the silver halide grains. Similar results are obtained when the above procedure is repeated with a pure silver chloride photographic emulsion. However, when the above procedure is repeated with silver halide grains in which the mole percent of chloride is reduced to 8 mole percent, the D_{max} of the emulsion is reduced by at least 10 percent. Similarly, the treatment of the silver halide grains with an iodide compound to bring the silver iodide content up to about 6 percent, increases the minimum density (D_{min}) exhibited by the emulsion at least five fold.

Example 2

The silver halide grains employed in the practice of this invention can be fogged with the combination of a reduction fogging agent and a gold fogging agent. To illustrate, a series of coatings are prepared as described in Example 1 except that one portion is fogged with both a reducing agent (9 mg. of thiourea dioxide per silver mole) and a gold salt (5 mg. of potassium chloroaurate per silver mole). The coatings are tested as described in Example 1 with the following results.

TABLE 2

Coating No.	g. of KBr added per mole silver	Relative Speed	Gamma	D_{max}	D_{min}	D_{max} Loss
1 (fogged with thiourea dioxide alone).....	4.5	224	4.9	4.4	.05	1
2 (fogged with both thiourea dioxide and potassium chloroaurate)....	4.5	166	4.6	4.83	.10	2

the scope of the invention unless otherwise specifically indicated.

Example 1

A photographic silver chlorobromide (46 mole percent chloride and 54 mole percent bromide) gelatin emulsion is prepared by adding a solution of silver nitrate to a gelatin solution containing potassium bromide and sodium chloride. The emulsion is fogged by the addition of 9 mg. of thiourea dioxide per mole of silver halide, adjusting the pH to 8.8 and heating for about 15 minutes at 165° F. The pH is adjusted to 4.5 and the emulsion is chill-set, shredded and washed in cold running water. The emulsion is melted, 10 cc. of a 10 percent aqueous formaldehyde solution per mole of silver halide is added, the pH adjusted to 8.8 and the emulsion further fogged by heating for about 15 minutes at 165° F. The emulsion is cooled to 110° F. and sufficient gelatin is added to give a gelatin content of 108 g. per silver halide mole. The emulsion is split into several portions. Potassium bromide is added to each portion in the amounts indicated in the following table to form a surface of silver bromide on the silver chlorobromide crystals. 30 cc. of a 10 percent aqueous formaldehyde solution per mole of silver halide is added as a hardener and each portion is coated on a conventional polyethylene terephthalate film support at a coverage of 410 mg. of silver halide per square foot of support. Samples of each coating are exposed on an intensity scale

Similar results are obtained when the above procedure is repeated with a silver chlorobromide photographic emulsion comprising 38 mole percent chloride and 62 mole percent bromide or a silver chlorobromiodide emulsion comprising 35 mole percent chloride, 62 mole percent bromide and 3 mole percent iodide.

Example 3

As previously pointed out herein, the fogged silver halide grains employed in the practice of this invention must comprise at least about 60 mole percent, and more preferably at least about 70 mole percent bromide in order to exhibit the required combination of resistance to kink and photographic properties.

To illustrate:

Emulsion A.—A photographic silver chlorobromide (65 mole percent chloride and 35 mole percent bromide) gelatin emulsion is prepared by adding a solution of silver nitrate to a gelatin solution containing potassium bromide and sodium chloride. The emulsion is fogged by the addition of 9 mg. of thiourea dioxide per mole of silver halide, adjusting the pH to 8.8 and heating for about 15 minutes at 165° F. The pH is adjusted to 4.5 and the emulsion is chill-set, shredded and washed in cold running water. The emulsion is melted, 10 cc. of a 10 percent aqueous formaldehyde solution per mole of silver halide is added, the pH adjusted to 8.8 and the emulsion further fogged by heating for about 15 minutes at 165° F. The emulsion is cooled to 110° F. and sufficient gelatin is

added to give a gelatin content of 108 g. per silver halide mole. Five grams of potassium bromide are added per mole of silver halide to form a surface of silver bromide on the silver halide to form a surface of silver bromide on the silver chlorobromide crystals. The halide content of these crystals is 48 mole percent chloride and 52 mole percent bromide.

Emulsion B.—A second fogged silver chlorobromide (20 mole percent chloride and 80 mole percent bromide) gelatin emulsion is prepared in the same manner as Emulsion A.

30 cc. of a 10 percent aqueous formaldehyde solution per mole of silver halide is added to each emulsion and each emulsion is coated on a conventional polyethylene terephthalate film support at a coverage of 410 mg. of silver halide per square foot. Samples of each coating are exposed on an intensity scale sensitometer and processed for 2 minutes in Kodak D-11 developer, fixed, washed and dried. Each of the coatings exhibit the same resistance to kink-mark desensitization. However, as shown by the following Table 3, the photographic properties of Emulsion B are significantly improved.

TABLE 3

Emulsion Coating:	Relative Speed	Gamma	D _{max}	D _{min}
A-----	100	4.5	4.7	0.19
B-----	340	5.3	5.5	0.04

From the above results it can be seen that the direct-positive silver halide Emulsion B comprising at least 60 mole percent bromide exhibits higher speed, gamma and D_{max} and lower D_{min} in comparison to the direct-positive silver halide Emulsion A having a bromide content below 60 mole percent while maintaining resistance to kink-mark desensitization.

Similar results are obtained when the potassium bromide is added to the silver halide crystals during fogging or after fogging and prior to coating.

Thus, by the practice of this invention there is provided a means for reducing the loss in D_{max} exhibited by fogged, direct-positive photographic silver halide emulsion layers upon physical deformation while at the same time improving their photographic properties.

Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected without departing from the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A direct-positive photographic emulsion comprising fogged silver halide grains in which at least about 60 mole percent of said halide is bromide, at least about 10 mole percent of said halide is chloride and less than about 5 mole percent of said halide is iodide, about 0.025 to about 0.5 mole of said bromide, per mole of silver, forming a surface on said grains.

2. A direct-positive photographic emulsion according to claim 1, in which at least about 20 mole percent of said halide is chloride and about 0.05 to about 0.3 mole of said bromide, per mole of silver, form a surface on said grains.

3. A direct-positive photographic emulsion according to claim 1, in which said silver halide grains are fogged with a reduction fogging agent.

4. A direct-positive photographic emulsion according to claim 1, in which said silver halide grains are fogged with a reduction fogging agent and a gold fogging agent.

5. A direct-positive photographic emulsion according to claim 4, in which said reduction fogging agent is thiourea dioxide and said gold fogging agent is potassium chloroaurate.

6. A photographic element comprising a support and at least one direct-positive photographic emulsion layer comprising fogged silver halide grains in which at about 60 mole percent of said halide is bromide, at least about 10 mole percent of said halide is chloride and less than about 5 mole percent of said halide is iodide, about 0.025 to about 0.5 mole of said bromide, per mole of silver, forming a surface on said grains.

7. A photographic element according to claim 6, in which said support is a polyester film support.

8. A photographic element according to claim 6, in which said support is a polyester film support, at least about 20 mole percent of said halide is chloride, at least about 60 mole percent of said halide is bromide and about 0.05 to about 0.3 mole of bromide, per mole of silver, forms a surface on said grain.

9. The method which comprises (1) reacting (a) photographic silver halide grains in which more than about 10 mole percent of said halide is chloride and less than about 5 mole percent of said halide is iodide with (b) a water soluble bromide salt to replace chloride on the surface of said grains, (2) stopping said reaction when the concentration of bromide in said grains is at least about 60 mole percent, the concentration of chloride in said grains is no less than about 10 mole percent and (3) fogging said grains.

10. The method according to claim 9 in which more than about 20 mole percent of said halide in (a) is chloride and said grains are fogged with a reduction fogging agent.

11. The method of claim 9 in which said water soluble bromide salt is potassium bromide and said grains are fogged with thiourea dioxide.

12. The method of claim 9 in which said water soluble bromide salt is employed at a concentration in the range of about 0.05 to about 0.3 mole of water soluble bromide salt per mole of silver.

13. The method which comprises (1) reacting (a) fogged photographic silver halide grains in which more than about 10 mole percent of said halide is chloride, at least about 40 mole percent of said halide is bromide and less than about 5 mole percent of said halide is iodide with (b) a water soluble bromide salt to replace at least about 0.015 mole of chloride per mole of silver, on the surface of said grains and (2) stopping said reaction when the concentration of chloride in said grains is no less than about 10 mole percent.

14. The method according to claim 13 in which at least about 20 mole percent of said halide in said fogged photographic silver halide grains of (2) is chloride.

15. The method of claim 13 in which said water soluble bromide salt replaces about 0.03 to about 0.2 mole of chloride, per mole of silver.

16. The method of claim 15 in which said water soluble bromide salt is potassium bromide.

17. A direct-positive photographic silver halide emulsion wherein the silver halide of said emulsion consists essentially of silver halide grains in which at least about 60 mole percent of said halide is bromide, at least about 10 mole percent of said halide is chloride and less than about 5 mole percent of said halide is iodide, about 0.025 to about 0.5 mole of said bromide, per mole of silver, forming a surface on said grains.

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NORMAN G. TORCHIN, Primary Examiner

U.S. Cl. X.R.

96—107, 109

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,477,852 Dated November 11, 1969

Inventor(s) Norman Allentoff and Henry Harrison Fogler

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 65, "exhibting" should read --exhibiting--.
Column 3, line 53, "solver" should read --silver--; line 65,
"2,944,987" should read --2,944,897--. Column 4, line 29,
"polyethyene" should read --polyethylene--. Column 7, line
42, "th" should read --the--. Column 8, Claim 8, line 16,
"grain." should read --grains.--; Claim 12, line 35, "sale"
should read --salt--.

SIGNED AND
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JUN 2 1970

(SEAL)

Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patent:

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