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## PHOTOGRAPHIC REDUCING COMPOSITION AND PROCESS

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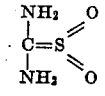
This invention relates to photographic compositions and more particularly to photographic processing solutions and to photographic processes for utilizing such compositions. In one of its more specific aspects it relates to photographic reducing solutions for treating silver salts and photographic processes utilizing such solutions. In some of its further aspects it relates to new chemical compositions for photographic development and toning.

This invention has for an object to provide new and useful reducing compositions for silver salts. A further object is to provide a reducing agent which can be used for the reduction of photographic images in alkaline, neutral or acid media. A still further object is to provide more effective and more economical reducing agents which can be used in acid media. A still further object is to provide new and useful developer solutions. Another object is to provide developer solutions for reversal processes. Yet another object is to provide a practical and economical means for toning a silver image to produce warm and pleasing brown to sepia toned images. Still other objects will be apparent from the following description of the invention.

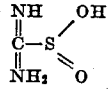
It has been found that the oxygenated reaction products of hydrogen peroxide with thiourea and certain of its hydrocarbon substitution products have considerable utility in photographic processing baths especially for reducing silver salts to metallic silver in photographic elements.

The exact structure of oxygenated reaction products of thiourea with hydrogen peroxide prepared from these reactants in neutral solution is not known with certainty. It has been called thiourea dioxide by some investigators which is indicative of a formula such as that set forth in (A) below. Others, however, have advanced the name imino-amino-methane-sulfinic acid and formamidine sulfinic acid which implies a structure having formula (B):

(A)



(B)



It is possible that both formulae may be equally correct, because the compound may exist in several desmotropic forms. It is possible that the compound exists in a desmotropic form wherein an equilibrium normally obtains between the two forms set forth above, which may undergo rearrangement depending upon whether the compound is in acid or alkaline medium, or upon physical characteristics such as temperature and pressure.

Furthermore, it is conceivable, considering the second formula, that it forms a salt when in alkaline solution e. g. the sodium sulfinate when in sodium hydroxide solution. It is further conceivable that in acid solution it forms salts on the imino group, for instance, a hydrochloride.

Since the utility of the compound in accordance with this invention does not depend upon the exact structure of the oxygenated reaction product of thiourea or hydrocarbon substituted thiourea with hydrogen peroxide, and for convenience, the names imino-amino-methane sulfinic acid or formamidine sulfinic acid will be used. The expression an imino-amino-methane sulfinic acid will be used to cover formamidine sulfinic acid and its derivatives which are capable of reducing silver salts.

To be more specific, it has been found that an imino-amino-methane sulfinic acid in aqueous solution and especially formamidine sulfinic acid is capable of preferential reduction of exposed silver halide grains in the presence of unexposed silver halides to give a photographic image so long as the solution is definitely acid. However, if the pH of the solution is increased toward neutral, the reduction potential of the compound increases, tending to give an overall blackening effect which is relatively weak at a pH of 6 but quite powerful at pH values in excess of 6.8.

The last mentioned effect is advantageously used in accordance with one aspect of the invention in reversal processes. The ordinary processes of preparing positive images by removal of a negative image, followed by reduction of the remaining silver halides in a reducing solution containing an imino-amino-methane sulfinic acid, can be carried out with or without a second exposure to light. The most convenient methods employ no second exposure, but merely consist of immersing the film, after the original image has been removed and the emulsion cleared and washed; in a solution containing sufficient formamidine sulfinic acid to reduce the silver salts to metallic silver. While acid solutions are useful, especially if re-exposure is resorted to, it has been found that alkaline solutions of an imino-amino-methane sulfinic acid have a powerful reducing action on exposed or unexposed silver halide grains. This is especially true of formamidine sulfinic acid.

In a further aspect of the invention an imino-amino-methane sulfinic acid is used in acid solution as the ordinary developer. Such solutions are capable of reducing the silver halide grains of an exposed photographic emulsion to form a metallic silver image. A silver halide emulsion containing latent images as formed by exposure to an original scene or by printing from a developed photographic element, is treated in an aqueous acid solution containing sufficient of an imino-amino-methane sulfinic acid to develop the exposed silver salts. Formamidine sulfinic acid developers, however, are preferred.

In still another aspect of the invention, aqueous acidic solutions containing small amounts of an imino-amino-methane sulfinic acid are used to redevelop a bleached silver image. A photographic element containing a bleached silver image is immersed in an aqueous acidic solution of the type described in sufficient amount to reduce the silver salts. The resulting image is characterized by various tones depending upon the particular pH value of the developer formula.

The treating solutions used in the processes outlined above may contain in addition to the imino-amino-methane sulfinic acid various modifying agents which are useful in developer solutions such as restrainers, preservatives, agents for controlling image tone, wetting agents, hardeners, materials whose presence retards the rate of diffusion of the solution in emulsion layers etc. The invention, however, is not limited to solutions, on the contrary, dry reducing compositions containing the specified ingredients with the exception of water are comprehended.

The invention will be further illustrated, but is not intended to be limited by the following examples. The first group consists of developer solutions useful for ordinary development of silver images or sepia toning by redevelopment. They can be made by admixing the ingredients in any desired order with water. Dry compositions can be made in a similar manner by admixing the components in dry forms.

EXAMPLE I

| | | |
|---|---|---|
| Formamidine sulfinic acid | grams | 18 |
| Sodium bisulfite | do | 36 |
| Potassium bromide | do | 6 |
| Water | milliliters | 1000 |

EXAMPLE II

| | | |
|---|---|---|
| Formamidine sulfinic acid | grams | 15 |
| Sodium bisulfite | do | 20 |
| Potassium bromide | do | 5 |
| Potassium metabisulfite | do | 6 |
| Water | milliliters | 1000 |

EXAMPLE III

| | | |
|---|---|---|
| Formamidine sulfinic acid | grams | 24 |
| Sodium bisulfite | do | 52 |
| Potassium bromide | do | 8 |
| Water | milliliters | 1000 |

EXAMPLE IV

| | | |
|---|---|---|
| Formamidine sulfinic acid | grams | 20 |
| Sodium bisulfite | do | 45 |
| Potassium bromide | do | 5 |
| Water | milliliters | 1000 |

EXAMPLE V

| | | |
|---|---|---|
| Formamidine sulfinic acid | grams | 10 |
| Potassium bromide | do | 3 |
| Potassium metabisulfite | do | 9 |
| Water | milliliters | 1000 |

EXAMPLE VI

| | | |
|---|---|---|
| Formamidine sulfinic acid | grams | 4.5 |
| Potassium bromide | do | 3 |
| Potassium metabisulfite | do | 4.5 |
| Water | milliliters | 1000 |

Alkaline developer solutions suitable for the second developer in producing images by reversal methods can be made by admixing the ingredients set forth in the following examples in any desired order.

EXAMPLE VII

| | | |
|---|---|---|
| Formamidine sulfinic acid | grams | 25 |
| Potassium sulfite | do | 50 |
| Potassium bromide | do | 30 |
| Sodium hydroxide | do | 20 |
| Water | milliliters | 1000 |

EXAMPLE VIII

| | | |
|---|---|---|
| Formamidine sulfinic acid | grams | 5 |
| Hydroquinone | do | 10 |
| Potassium carbonate | do | 30 |
| Potassium sulfite | do | 50 |
| Water | milliliters | 1000 |

EXAMPLE IX

| | | |
|---|---|---|
| Formamidine sulfinic acid | grams | 30 |
| Sodium sulfite | do | 55 |
| Potassium bromide | do | 38 |
| Sodium hydroxide | do | 25 |
| Water | milliliters | 1000 |

EXAMPLE X

| | | |
|---|---|---|
| Formamidine sulfinic acid | grams | 36 |
| Sodium carbonate | do | 50 |
| Sodium sulfite | do | 40 |
| Water | milliliters | 1000 |

EXAMPLE XI

| | | |
|---|---|---|
| Formamidine sulfinic acid | grams | 8 |
| Potassium bromide | do | 15 |
| Sodium hydroxide | do | 15 |
| Water | milliliters | 1000 |

The amount of formamidine sulfinic acid is not limited to that set forth in the above examples but may be varied over a wide range. The amount to be used varies somewhat in accordance with the material treated.

*Acid development*

In the acid reduction or development procedures a range of concentrations from about 0.5% to 2.0% by weight of formamidine sulfinic acid in respect to the final weight of the solution represents a practical range. N-hydrocarbon substituted formamidine sulfinic acids can be used in like amounts.

The compositions of the acid baths should be balanced so that the pH value of the developing bath is from pH 3 to pH 6. Values higher or lower than those given will usually produce poor results, a higher pH tending to produce a fog and too low a pH slowing down the reducing action to an unworkable extent. By proper adjustment both negative and positive plates, films and papers can be satisfactorily developed. The pH concentrations can be adjusted by the addition of various acidic or alkaline materials or compounds such as lactic acid, glycollic acid, sodium acetate, sodium amino acetate, sodium citrate, boric acid, etc.

*Toning development*

Redevelopment of a bleached silver image as above described in an imino-amino-sulfinic acid

developer of the acidic type especially aqueous formamidine sulfinic acid developers, has a surprising and unexpected effect on the color of the image produced. Instead of the normal image tones obtained by the development of an original exposed but undeveloped emulsion, the bleached image reappears in brownish to sepia tone values. Any one of the common bleaching baths known to the art may be used, such as ferricyanide-bromide or copper sulfate-chloride bleaches. A developed film, plate or paper print which has been fixed and thoroughly washed is simply immersed in a bleaching bath until the image is thoroughly bleached and is then washed and transferred to a bath containing a developing bath of formamidine sulfinic acid. After a short time the image reappears in brownish to sepia tones which may be varied by changes in the developing bath. A more convenient method of varying the tone values, however, can be used in which the original image is first bleached, then washed, then developed in a dilute metol-hydroquinone developer, neutralized in an acid stop bath after partial redevelopment and then transferred to a formamidine sulfinic acid developer to complete the redeveloper. The first part of the development in an ordinary alkaline developing bath converts parts of the latent image to metallic silver and the rest is converted to brown silver salt by the formamidine sulfinic acid bath. By varying the length of time the emulsion is in each bath, many different intermediate tones between brown and black may be produced. The amount of imino-amino-methane sulfinic acid has some effect on the image color. In general, the higher the concentration the darker the image. Amounts from 0.5% to 2.0% by weight of the sulfinic acid in respect to the final weight of the solution gives satisfactory results. However, lesser amounts and amounts in excess of 2.0% may be used.

Various other developing agents can be used in place of the metol-hydroquinone developer. Suitable agents include chlorohydroquinone, 2:4-diaminophenol hydrochloride and p-hydroxyphenyl amino acetic acid.

*Reversal development*

Various procedures can be used in this phase of the invention. In general, however, an exposed film, plate or paper print is developed according to the usual procedure known to the art and then bleached in an acid solution of potassium bichromate which removes the silver image. After washing and clearing in a sodium bisulfite solution, the photographic element is then transferred to an alkaline solution of formamidine sulfinic acid such as those described in Examples I and VI. This bath rapidly reduces all the silver halide which was not originally affected by the light and bleached out after development. Consequently a reversed image is produced which may be fixed, hardened and washed to give a positive image of the original subject. An alkaline formamidine sulfinic acid solution to be used in such a process should preferably contain from about 0.5% to 3% by weight of formamidine sulfinic acid. For best results the pH of such solution should be above 9.5.

Other N-hydrocarbon substituted imino-amino-methane sulfinic acids which are capable of reducing silver salts, can be used in the above described procedures and compositions in similar amounts. Suitable substituents include lower alkyl groups, e. g. methyl and ethyl; aryl radicals, e. g. phenyl, chlorphenyl, etc. Suitable substituted compounds include N-methyl formamidine sulfinic acid, N-ethyl formamidine sulfinic acid, N-alkyl formamidine sulfinic acid, N-phenyl formamidine sulfinic acid and N-chlorophenyl formamidine sulfinic acid which can be made from the corresponding N-hydrocarbon substituted thiourea and hydrogen peroxide.

In place of all or a part of the specific preservatives, set forth in the above examples, can be substituted one or more other sulfites, bisulfites, etc. Suitable additional compounds of this type include lithium, ammonium, substituted ammonium and amine salts of sulfurous acid, e. g. triethanolamine-, morpholine-, tetramethylammonium-, and trimethylbenzylammonium sulfites. A portion of the bisulfites can be replaced by lithium sodium, potassium and ammonium bisulfites and meta bisulfites. Other compounds include acetone bisulfites, formaldehyde sodium sulfoxylate, hexahydric alcohols and lactic and glycollic acids.

Similarly in place of the specific restrainers of the above examples which can be interchanged in any desired manner, can be substituted one or more other compounds of this type. Suitable other compounds include, sodium and lithium bromides, chlorides, and iodides potassium chloride and iodide, ammonium bromide, etc.

Agents for controlling the image tones can be incorporated with the novel reducing agents hereof. Among the useful agents are quinone hydrochloride, quinoline, 5-nitrobenziminazole, triazole, benztriazole, iminazole, pseudo thiohydantoin, indophenyl iodonium chloride, etc.

Compounds which retard the rate of diffusion of solutions through emulsion layers, e. g. sugar, etc., may be added to the reducing compositions. Similarly wetting agents such as the sodium salts of alkyl sulfates and alkyl sulfonic acids of 8 to 18 carbon atoms; C- and N- alkyl betaines wherein the alkyl groups contain 8 to 18 carbon atoms, etc. can be used in the compositions and procedures. Also emulsion hardeners such as potassium aluminum sulfate and chrome alum have a useful hardening action in solutions of low pH. Aldehyde hardeners are useful in alkaline or neutral solution.

The developer or reducing solutions of this invention are useful in developing various types of photographic elements such as camera, cinema, portrait, lithographic and X-ray, films and plates and photographic papers, etc. They are useful with various types of film base materials and do not have a deleterious effect thereon. Thus cellulose derivative film bases, e. g. cellulose nitrate, methyl cellulose, ethyl cellulose acetate, cellulose acetate-propionate and cellulose ester and ether film bases, in general; synthetic resins, e. g. polyvinyl acetals, etc.; and super polymers, e. g. nylon, may form part of the elements treated.

Various types of silver halide emulsion layers may be treated as will be apparent from the above. For instance, simple and mixed silver chloride, silver bromide, silver iodide, silver chloride-bromide, and silver chloride-bromide-iodide, gelatin emulsion layers, may be satisfactorily processed by the novel solutions and procedures hereof.

The reducing solutions can be used with various types of colloid binding media. They do not have harmful effects on gelatin, agar agar, albumins, synthetic resins, e. g. polyvinyl acetals

used as the binding agents for the silver salts.

The baths can be used over a fairly wide range of temperature with complete safety. In addition, they have a fairly long useful life throughout practical processing temperatures.

One of the most important advantages of the invention is that formamidine sulfinic acid is a much more energetic photographic reducing agent in both acid and alkaline solutions than are the compounds already employed in the art. Overall blackening by alkaline solutions in reversal processes is likewise more easily and quickly obtained by the compound of the invention than by equivalent quantities of hydrosulfites or sulfoxylates. Another advantage of the invention is that it permits the formation of brownish to sepia toned images having wide gradation of color from reddish brown to brownish black by partial redevelopment of a bleached silver image in an ordinary developer and completing the redevelopment in a formamidine sulfinic acid developer.

As many apparently widely different embodiments of this invention may be made, without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments hereof except as defined by the appended claims.

We claim:

1. A photographic reducing solution containing a water soluble sulfite and an imino-amino-methane-sulfinic acid.

2. A dry photographic reducing composition containing a water soluble sulfite and an imino-amino-methane-sulfinic acid.

3. An aqueous acidic photographic reducing solution containing a water soluble sulfite and an imino-amino-methane-sulfinic acid.

4. An alkaline photographic reducing composition containing an alkaline compound, a water soluble sulfite and an imino-amino-methane-sulfinic acid.

5. A dry photographic reducing composition containing an alkaline compound, a water soluble sulfite and an imino-amino-methane-sulfinic acid.

6. An aqueous photographic reducing solution containing a water soluble sulfite and formamidine sulfinic acid.

7. An aqueous acidic photographic reducing solution containing a water soluble sulfite and formamidine sulfinic acid.

8. An alkaline photographic reducing solution containing an alkaline compound, a water soluble sulfite and formamidine sulfinic acid.

9. The process which comprises reducing a light sensitive photographic element in an aqueous solution containing an imino-amino-methane-sulfinic acid.

10. The process which comprises developing a photographic element containing a silver salt layer in an aqueous solution containing formamidine sulfinic acid.

11. In a photographic reversal process involving a first development and bleaching of developed images, the step which comprises developing the reversed image in an aqueous solution containing an imino-amino-methane-sulfinic acid.

12. A photographic process for obtaining direct positives which comprises effecting a first development, removing the silver image formed and effecting a final reduction of the remaining silver salt in an aqueous solution containing an imino-amino-methane-sulfinic acid.

13. A photographic process for obtaining direct positives which comprises effecting a first development, removing the silver image formed and effecting a final reduction of the remaining silver salt in an aqueous solution containing formamidine sulfinic acid.

14. A photographic process for obtaining direct positives which comprises effecting a first development, removing the silver image formed and effecting a final reductilon of the remaining formsalt in an alkaline solution containing formamidine sulfinic acid.

15. A photographic process for obtaining direct positives which comprises effecting a first development, removing the silver image formed and effecting a final reduction of the remaining silver salt in an alkaline solution containing an imino-amino-methane sulfinic acid.

16. A photographic process for obtaining direct positives which comprises effecting a first development, removing the silver image formed and effecting a final reduction of the remaining silver salt in an alkaline solution containing formamidine sulfinic acid having a pH in excess of 6.8.

17. The process of producing reddish brown to sepia tones in a photographic silver image which comprises redeveloping a bleached silver image in an aqueous solution containing an imino-amino-methane-sulfinic acid having a pH less than 6.0.

18. The process of producing reddish brown to sepia tones in a photographic silver image which comprises redeveloping a bleached silver salt image in an aqueous solution containing formamidine sulfinic acid having a pH less than 6.

19. The process of toning which comprises partially developing a bleached image with an ordinary developing agent and completing the development in an aqueous solution containing an imino-amino-methane-sulfinic acid.

20. An alkaline photographic reducing composition containing an alkaline compound, a water soluble sulfite, and formamidine sulfinic acid.

21. An alkaline photographic reducing composition containing sodium hydroxide, an alkali metal sulfite and formamidine sulfinic acid.

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