Patented May 16, 1939

2,158,185

UNITED STATES PATENT OFFICE

2,158,185

TONING AND INTENSIFYING SOLUTIONS

Kenneth C. D. Hickman and John C. Hecker, Rochester, N. Y., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

No Drawing. Application March 9, 1938, Serial No. 194,899

5 Claims. (Cl. 95—88)

This invention relates to toning and intensifying solutions for developed photographic images, whether in the form of negatives or prints, and more particularly to a new type of single solution toning and intensifying bath.

This application is in part a continuation of our copending application Serial No. 722,730, filed April 27, 1934.

As is well known, silver salts will react with other soluble salts, but metallic silver is attacked most readily by elementary substances or their equivalents. It is for this reason that one of the best known methods of sulfide toning involves first, the conversion of the metallic silver to a salt, such as silver bromide and potassium ferricyanide and, second, the conversion of the silver bromide to silver sulfide by double decomposition with sodium sulfide. This particular conversion, however, cannot be made in one stage in a single solution because the ferricyanide attacks the sodium sulfide more readily than the silver. The problem is then to find an oxidizing agent sufficiently powerful to oxidize the silver and yet be compatible with the sulfiding agent. A number of single solution sulfide toning processes have been developed to solve this problem, but each suffers some drawback. In the well known hypo-alum process, for example, the bath draws sulfur from the hypo and oxidizer from the air, but the solution must be heated and the process is slow. Other sulfide toning baths comprising sodium or barium sulfide and sodium meta-nitrobenzene sulfonate are slow in action and vile in odor.

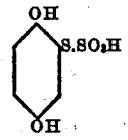
It is the principal object of the present invention to provide a single solution toning bath which will meet many of the requirements of such baths without at the same time possessing the limitations of the hitherto known solutions. A further object is to provide a single solution bath which may not only be used for toning the image, but also for intensification. A still further object is to provide a bath of this type possessing the novel property that it may be employed for toning a photographic image immediately after development and before fixing. With the above and other objects in view which will become apparent as the description proceeds, we have set forth our invention in the following specification and examples which are included merely for purposes of illustration and not as a limitation thereof.

We have discovered that various soluble thiosulfates may be employed for the toning and intensification of silver images. These compounds are characterized by the fact that they all contain available sulfur in their di-valent condition. Many other substances contain di-valent sulfur, mostly the thioureas and the polysulfides, but in such compounds the di-valent sulfur is connected to an unlike atom or to another unsaturated sulfur atom. The di-valent sulfur in the class of compounds considered within the scope of this invention is connected by one or two bonds to another sulfur atom, which latter atom is otherwise fully oxygenated and is in its hexa-valent condition. We shall discuss herein the thiosulfate derivatives, in particular the compounds of thiosulfuric acid and organic substances containing a quinone or hydroquinone grouping. In these discussions we shall refer to some of the broader theoretical aspects of our discovery, although we are not to be understood as in any way limiting our invention thereby.

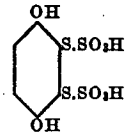
We have found that the silver salts of certain of these organic thiosulfuric acid derivatives readily eliminate silver sulfide. This is of especial importance, since in order to be suitable for use in a toning solution, the toning agent must be of the kind which will produce a silver salt which will readily decompose into silver sulfide as fast as the metallic silver is oxidized, as otherwise the image will wander or suffer reduction. Specifically we have found that they possess at one and the same time a greater instability toward acid and oxidizing agents and a greater stability toward silver with the result that their silver salts, which are more easily formed, are also more easily broken up, depositing silver sulfide, and therefore that such derivatives may be employed as toners with excellent results.

Among these derivatives may be mentioned the quinone and hydroquinone derivatives of thiosulfuric acid. Of the hydroquinone compounds, hydroquinone monothiosulfuric acid, hydroquinone dithiosulfuric acid and hydroquinone tetrathiosulfuric acid may all be formed by the reaction of a thiosulfate and quinone under controlled conditions. The conditions are not difficult to obtain and the acids are all easily prepared; the "mono" form resulting from dropping quinone dissolved in dilute acetic acid into ordinary hypo, the "di" form by adding hypo to quinone in acetic acid, while the "tetra" form separates in almost theoretical yield when solutions of chromic acid and hypo are added simultaneously to a solution of quinone in acetic acid. These three hydroquinone thiosulfuric acids are

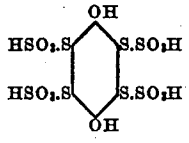
considered to have the following structural formulas:



Hydroquinone monothiosulfuric acid



Hydroquinone dithiosulfuric acid



Hydroquinone tetrathiosulfuric acid

It will be seen that each acid contains sulfur in the condition specified above as important to this invention, namely, attached to another fully oxygenated sulfur atom.

To form a toning bath, the hydroquinone compounds must be oxidized to the quinone form, or must be mixed with quinones or other oxidizing agents. Suitable oxidizing constituents of a toning bath, by way of example, are ordinary (benzo) quinone or potassium dichromate and an excellent toning bath for bromide and other developing out papers according to our invention, has the following composition:

Hydroquinone tetrathiosulfuric acid	g.	.5
Quinone	g.	1.0
Sulfuric acid	cc.	.25
Water	cc.	100.00

The above bath can be used continuously until the concentration of hydroquinone produced in the toning reaction becomes so high that an equilibrium mixture results which is non-reactive. The activity of the bath can then be restored, by adding chromic acid, although the rejuvenated bath stains slightly from dyes produced by secondary oxidation.

A toning bath containing as much as 1 per cent of free mineral acid may have a somewhat harmful effect on gelatine emulsions. Therefore, films and prints to be intensified in such a bath should be fixed in hypo containing alum and the toning solution should likewise be loaded with alum. Bearing in mind that hydroquinone is a product of the toning reaction, the toning solution in use may contain, in accordance with our invention, a quinone thiosulfuric acid, a hydroquinone, a mineral acid, and an alum, for example, chrome alum, potassium chromium sulfate. Such a solution containing chiefly the mono- and di-thiosulfuric acids, which confer both toning and intensifying properties may be made by mixing hydroquinone, chromic acid, and hypo—chemicals which are readily available in the photographic laboratory. Inasmuch as the toning solution does not keep well, its constituents should be bottled separately, a convenient recipe being as follows:

Solution A

Water	c.c.	500
Potassium dichromate	g.	16
Sulfuric acid (conc.)	g.	17

Solution B

Water	c.c.	500
Hydroquinone	g.	16
Sodium bisulphite	g.	.75

Solution C

Water	c.c.	500
Hypo	g.	11

Solution C'

Water	c.c.	350
Hypo	g.	80

Equal portions of the first three solutions are employed, B being poured into A in a thin stream with rapid stirring, after which C is added to the mixture, also with stirring. The resulting solution is then cooled down to below 70° F. for use.

If a quicker bath is needed, one tenth the volume of Solution C' may replace Solution C. A very vigorous bath may, for example, have the following formula:

Hydroquinone dithiosulfuric acid	g.	.5
Quinone	g.	1.0
Sulfuric acid	g.	.25
Water	c.c.	100.00

This solution should be used at about 65–75° F.

An example of a toning bath containing hydroquinone monothiosulfuric acid has the following composition:

Quinone	g.	1.0
Water	c.c.	100.00
Sulfuric acid	c.c.	0.25
Hydroquinone monothiosulfuric acid (conveniently in the form of its potassium salt)	g.	0.5

This toning solution produces a reddish-purple tone which can be varied by varying the quantity of the hydroquinone salt as desired.

While we do not wish to confine ourselves to any particular theory or explanation of the mechanism involved in the various reactions in toning by means of these hydroquinone thiosulfuric acids, we believe that the first product of toning is not silver sulfide, but a silver hydroquinone thiosulfate, for example, silver hydroquinone dithiosulfate in the case of a solution such as indicated in the preceding paragraph. This salt is creamy white and very insoluble, but in the presence of the excess oxidizing agent and acid soon changes to a greenish black. This compound which constitutes the toned or intensified image we believe to be the silver salt of a complex dye formed by acid oxidation from the hydroquinone dithiosulfate. The reactions taking place with the "mono" and "tetra" forms of the hydroquinone thiosulfuric acid are, we believe, similar to those occurring with the "di" form. The first stage in all the reactions is a bleaching of the image by virtue of formation of the silver salt of the hydroquinone acid employed. The second stage is the darkening of this compound by other substances in solution, the first development of color, probably being due to the formation of a quinhydrone. The third stage is a process occurring simultaneously with the other two, but at a rate varying with the nature of the solution, being the splitting off of silver sulfide from the silver thiosulfate chain.

One of the remarkable properties of our toning baths is that they can be adapted to tone the

image immediately after development and before fixing. This is due to the fact that the solubility of the first stage toning product is just less than that of the silver halides which permits the metallic silver to be converted to silver sulfide under conditions where silver halide remains substantially unattacked.

Toning.—Where toning of a print or film, as distinguished from intensification, is desired, the print (or film) after double fixation and a ten-minute wash to assure the removal of all soluble silver compounds, is immersed in a bath such as described above in connection with bromide prints, and containing, for example hydroquinone tetrathiosulfuric acid, and rocked gently until toning is complete. The bath is rich in volatile quinone and should the vapor tend to escape, the tray can be covered with a sheet of glass or Celluloid. The print should then be washed for about 45 minutes to remove the yellow coloration of the whites produced by the quinone. If not completely removed in this way, the yellow color may be eliminated by immersion in a 2% solution of sodium bisulfite at the end of the first ten minutes of washing.

Intensification.—The print or film to be intensified is first placed in a new unused bath containing 10–20% of plain hypo for five minutes. It is then washed for ten minutes and placed in a bath such as described above and containing, for example, hydroquinone di-thiosulfuric acid, quinone, alum and acid. Two or three minutes are generally required before the reaction is well under way, but when once started can lead to an increase in density of as much as 3 to 5 times in the course of a half hour. The photograph should then be washed for 10–15 minutes.

The colors of the toned image with the hydroquinone thiosulfuric acid toners will vary from brown to a greenish black. The actual color produced varies with the relative quantities of reagents in the bath and with the nature of the particular thiosulfuric acid employed.

We have found that many quinones and substituted quinones can yield thiosulfuric acid derivatives and all form toners with more or less desirable properties. Thus, the mono- and dichloro quinones yield thiosulfuric acids conferring a purple tone to silver images. The anthraquinones and the methyl-quinones give thiosulfuric acids, the usefulness of which is somewhat impaired by their sparing solubility, but, nevertheless, they come within the broad scope of our invention.

We give below further typical examples of our invention in which substituted quinone thiosulfuric acids are employed in the preparation of single solution toning and intensifying baths:

I. Monochloroquinone monothiosulfuric acid ---------- g-- 1
Sulfuric acid ---------- g-- .25
Water ---------- c. c-- 100

II. Methyl quinone monothiosulfuric acid ---------- g-- 1
Sulfuric acid ---------- g-- .25
Water ---------- c. c-- 100

Although in the above description we have referred mainly to toning and intensifying baths containing a single quinone or hydroquinone thiosulfuric acid as the essential toning and intensifying constituent, it will be evident that we may employ a plurality of these acids if desired.

As previously indicated, in those cases where a quinone thiosulfuric acid is employed, it is not essential to employ an oxidizing agent due to the fact that the quinone thiosulfuric acid acts as its own oxidizing agent. With the hydroquinone thiosulfuric acids, on the other hand, it is essential to employ an oxidizing agent. Furthermore, these thiosulfuric acids may be used, either in the form of the acid itself or in the form of a soluble salt, such as the sodium or potassium salt, it merely being a matter of convenience as to which form is employed.

What we claim is:

1. The process of toning and intensifying a developed silver image in a photographic film which comprises treating said image with an aqueous single solution toning and intensifying bath containing as its essential toning and intensifying constituent a substituted quinone thiosulfuric acid.

2. The process of toning and intensifying a developed silver image in a photographic film which comprises treating said image with an aqueous single solution toning and intensifying bath containing as its essential toning and intensifying constituent a substituted quinone monothiosulfuric acid.

3. The process of toning and intensifying a developed silver image in a photographic film which comprises treating said image with an aqueous single solution toning and intensifying bath containing as its essential toning and intensifying constituent a halogen-substituted quinone monothiosulfuric acid.

4. The process of toning and intensifying a developed silver image in a photographic film which comprises treating said image with an aqueous single solution toning and intensifying bath containing as its essential toning and intensifying constituent monochloroquinone monothiosulfuric acid.

5. The process of toning and intensifying a developed silver image in a photographic film which comprises treating said image with an aqueous single solution toning and intensifying bath containing as its essential toning and intensifying constituent methylquinone monothiosulfuric acid.

KENNETH C. D. HICKMAN.
JOHN C. HECKER.