Patented Apr. 12, 1949

2,467,359

UNITED STATES PATENT OFFICE

2,467,359

PHOTOGRAPHIC OXIDIZERS AND RESISTS

Leon Rubinstein, New York, N. Y.

No Drawing. Continuation of application Serial No. 453,671, August 5, 1942. This application January 23, 1946, Serial No. 642,981

12 Claims. (Cl. 95—88)

1

My present invention relates to photographic oxidizers and photographic resists adapted to be used in combination with these oxidizers.

The main fields of application for which my new oxidizers and resists are to be used are described in my prior application Serial No. 453,671, filed August 5, 1942, now abandoned, entitled "Oxidizers and resists," of which the present application is a continuation. My patent application Serial No. 453,671, filed August 5, 1942, is in turn a continuation-in-part of my U. S. application Serial No. 352,517, filed August 14, 1940, now abandoned, entitled "Screens and process of producing the same."

It is an object of my present invention to provide oxidizers adapted to form simultaneously a screen on photographically exposed and developed light sensitive emulsions for black and white, especially for color separation pictures and color transparencies and to correct the transparency of these pictures.

Another object of my invention is to use my new oxidizers for retouching photographic pictures of different kinds as for instance black and white, especially color separation pictures and color transparencies produced by additive and subtractive color photographic processes, X-ray plates, motion picture negatives and lantern slides.

Still another object of my present invention consists in new photographic resists especially well adapted to resist action of the new oxidizers proposed herewith.

A further object of my present invention consists in oxidizers which do not destroy the details of the treated pictures and which are furthermore inexpensive and storable for a practically unlimited time.

Still a further object of my present invention is to use my new oxidizer for half tone dot etching; with this new oxidizer, the dot etching process is much simpler, easier to control, and gives much better results than other known processes.

Further objects and advantages of the invention will be set forth in the following specification and in part will be obvious therefrom without being specifically pointed out, the same being realized and attained as hereinafter more particularly described or as pointed out in the claims hereof.

With the above and other objects of my invention in view, my present invention mainly consists in new oxidizers which comprise as main elements at least one substance of the halogen

2

group and at least one substance of the group of aldehydes.

The halogen used has the main oxidizing effect while the aldehyde has a preserving effect and furthermore enables control of the photographic contrasts of the picture. In most cases, it is preferable to add to the new oxidizers also a substance selected from the group of hydrochloric, sulphuric, and nitric acids, as such substances expedite the oxidizing process and also preserve the oxidizers, thereby making it storable for a practically unlimited time.

The term "aldehyde," as used throughout the specification and claims, is intended to cover all compounds containing the CO-radical attached to both a hydrogen atom and a hydrocarbon radical; such compounds are, for instance, formaldehyde, furfuraldehyde, and acetaldehyde. Finally, the acid group mentioned above is intended to include not only the hydrochloric, sulphuric, and nitric acids themselves but all derivatives and compounds of these acids which have, when used in the oxidizer mixture, the same expeditive and preserving effects.

I have found that I can use as oxidizers for producing screens of the character described in my U. S. Patent application Serial No. 352,517, and for other photographic contrast controlling and retouching purposes compositions of matter comprising at least one substance of the halogen group, preferably iodine or bromine, at least one aldehyde, preferably formaldehyde, and at least one acid selected from the group consisting of hydrochloric, sulphuric, and nitric acids; these substances have to be dissolved in water or glycerine, according to the different purposes for which they are to be used.

I have furthermore found that for producing screens, it is preferable to use an oxidizer comprising about one to two parts by volume of at least one substance selected from the group consisting of iodine tinctures and concentrated iodine solutions, about one to two parts by volume of an iodine of the decolorized iodine group, about one to two parts by volume of an aqueous solution containing about 40% of formaldehyde, and about one to two parts by volume of an acid selected from the group consisting of hydrochloric, sulphuric, and nitric acids and their derivatives, said iodines, formaldehyde and acid being dissolved in about 120 parts by volume of distilled water.

In order to control the formation of the screen on the gelatinous surface, i. e. to vary the softness or contrasts of the screen pattern, I may

add sugar or common salt, i. e. sodium chloride, to the above described oxidizer. I have found that by adding these substances and varying the added quantity I am able to produce screen-like corrugations of different softness and contrasts. Furthermore, I have found that it is of advantage for local retouching purposes, in which case a strong oxidizer is needed, to dissolve the iodine, formaldehyde and acid not in water but in glycerine or the like, thus forming an oxidizing solution that acts quickly and vigorously.

In the following are described different oxidizer solutions which I have found especially advantageous for my purposes:

(1) A preferred oxidizer which has proved to be the best for substantially all my purposes consists of:

Concentrated iodine	drams	1
Decolorized iodine N. F. VI	do	3
Formalin	do	1
Hydrochloric acid (or sulphuric or nitric acid)	dram	1
Common salt or sugar	oz	2
Distilled water	oz	16

The decolorized iodine N. F. VI, as described by the 6th edition of The National Formulary of the American Pharmaceutical Association, comprises a solution of 25 gms. of potassium iodide in 400 cc. of water to which is added 50 gms. of iodine and 400 cc. of alcohol. After the iodine is completely dissolved, 100 cc. of strong ammonia water is added and the mixture allowed to stand until it becomes colorless. Thereafter sufficient alcohol is added to make the product measure 1000 cc.

I propose to make this oxidizer by first adding half of the water to the acid and separately mixing the concentrated iodine with the decolorized iodine, and thereafter combining the two solutions; then the formalin and the salt or sugar are added and the solution shaken until the salt or sugar is completely dissolved and finally the rest of the distilled water is added.

The concentrated iodine used is preferably a saturated iodine solution. I produce this saturated iodine solution by dissolving one ounce of crystalline iodine and one ounce of crystalline potassium iodide in 8 ounces of a 10 per cent aqueous solution of potassium iodide until this potassium iodide solution is saturated with iodine. After being filtered, this solution may be used for the oxidizer.

(2) Another preferred oxidizer solution consists of:

Concentrated iodine solution	drams	1
Decolorized iodine N. F. VI	do	3
Formalin	do	3
Hydrochloric acid (or sulphuric or nitric acid)	drams	2
Common salt or sugar	oz	2
Distilled water	oz	16

This solution is most advantageously used for extremely dense color transparencies where no white objects are visible.

I prefer to make this oxidizer by mixing the concentrated iodine with half of the water, separately mixing the decolorized iodine with the formalin, and thereafter combining the two mixtures; thereafter the acid and the salt or sugar are added and the solution is shaken until the heavy particles in the solution disappear and the solution becomes clear. Then the second half of the water is added. No filtering is necessary; the oxidizer is ready for use.

I want to stress that the ozidizer solutions described above are those preferred by me for the purposes of the present invention; these oxidizers are made with concentrated iodine solution, prepared as described above. I have found that this concentrated iodine is the most advantageous for my oxidizers.

(3) For color transparencies, I prefer to use an oxidizer solution comprising:

Tincture of iodine U. S. P.	drams	3
Decolorized tincture of iodine N. F. VI	do	3
Formalin	do	1–3
Hydrochloric acid (or sulphuric, nitric or other equivalent acid)	drams	2
Distilled water	oz	16

If this solution is to be used on paper prints, two ounces of common salt or sugar should be added, except when using nitric acid, in which case salt or sugar should not be added. I propose to make this oxidizer by first placing the acid in a bottle and slowly pouring into this bottle the distilled water, then mixing this acid solution with the tincture of iodine, the decolorized iodine and the formalin, and adding thereafter the second half of the water. No filtering is necessary.

(4) For the same purpose, I can also use an oxidizer solution comprising:

Tincture of iodine U. S. P	drams	3
Decolorized tincture of iodine N. F. VI	drams	3
Formalin	do	1 to 3
Hydrochloric acid (or sulphuric, nitric or other equivalent acid)	dram	3
Distilled water	oz	7

For use on paper prints in order to produce softer color effects, about 1 ounce of salt may be added, except when using nitric acid for the oxidizer. I prefer to produce this oxidizer solution by first mixing the iodine with the formalin and then adding the water to the mixture thus produced; after this solution is filtered, first the acid is added and then the salt.

(5) Another oxidizer solution found to be very useful comprises:

Tincture of iodine U. S. P	drams	3
Decolorized tincture of iodine N. F. VI	drams	3
Formalin	do	1 to 3
Hydrochloric acid (or sulphuric, nitric or other equivalent acid)	dram	1
Distilled water	oz	7

This oxidizer is prepared in substantially the same way as described above. Use of decolorized tincture of iodine N. F. VI makes the above described filtering step unnecessary.

(6) As a soft oxidizer working very well on color transparencies and on prints, I prefer to use an oxidizer comprising:

Iodine test solution (T. S. U. S. P.)	drams	2 or 3
Potassium iodide test solution (T. S. U. S. P.)	do	1
Sulphuric acid (or hydrochloric, nitric or other equivalent acid)	do	1
Distilled water	oz	7

The iodine test solution above referred to is

a tenth-normal iodine solution. The potassium iodide test solution consists of .5 gm. of iodine and 1.5 gm. of potassium iodide dissolved in 25 cc. of distilled water.

(7) Another oxidizer that also works well is the following:

Iodine test solution (T. S. U. S. P.)	drams	1½
N. P. decolorized iodine	do	1½
Hydrochloric acid (or sulphuric or nitric acid)	do	1
Tincture of iodine (U. S. P.) alcohol 83%	do	2
Formalin	do	2
Distilled water	oz	14

I prepare this oxidizer by first mixing the iodine test solution with half of the water, adding to this solution the decolorized iodine, the acid, the potassium iodide test solution, the tincture of iodine and the formalin, and thereafter the rest of the water. This solution works very well but becomes decolorized within about 6 to 10 days and cannot be further used. If it becomes decolorized, however, iodine test solution may be added to revive the solution to its former strength.

(8) Another very useful but not durable oxidizer solution consists of:

Churchill's tincture of iodine N. F. alcohol 62%	drams	½
Decolorized tincture of iodine N. F. IV	do	1
Formalin	do	1
Hydrochloric acid (or sulphuric or nitric acid)	do	1
Common salt or sugar	oz	1
Distilled water	oz	14

Churchill's tincture of iodine is an alcoholic solution of iodine and potassium iodide containing not less than 16 gm. and not more than 17 gm. of iodine and not less than 3 gm. and not more than 4 gm. of potassium iodide in each 100 cc.

The decolorized iodine N. F. IV, as described by the 4th edition of The National Formulary of the American Pharmaceutical Association, comprises a solution in 100 milliliters of water of 83 gms. of iodine and 83 gms. of sodium thiosulphate. Thereafter 125 milliliters of alcohol are added and after the addition of the alcohol, 65 milliliters of strong ammonia water. After the mixture has cooled and become colorless, sufficient alcohol is added to make the product measure 1000 milliliters.

(9) Still another oxidizer adapted for my purposes consists of:

Solution iodine compound (Lugol) U. S. P	drams	1
Decolorized tincture of iodine N. F. VI	do	2
Formalin	do	2
Hydrochloric acid (or sulphuric or nitric acid)	do	2
Distilled water	oz	14

Lugol's solution of iodine compound is the standard U. S. Pharmacopoeia solution and is defined as a solution containing in each 100 cc. not less than 4.5 gm. and not more than 5.5 gm. of iodine and not less than 9.5 gm. and not more than 10.5 gm. of potassium iodide.

(10) For half-tone dot etching, I may use an oxidizer solution consisting of:

		Ounces
Any of the above described iodine oxidizer solutions		8
Iodine		about 2½
Formalin		about 2½
Hydrochloric acid (or sulphuric or nitric acid)		about 2½

This oxidizer is much stronger than the above described ones and therefore especially adapted for dot etching purposes.

(11) Still another oxidizer giving very good results consists of:

Iodine	drams	6
Acetaldehyde	do	1 to 3
Hydrochloric acid (or sulphuric, nitric or other equivalent acids)	do	1 to 2
Distilled water	oz	8 to 16

This oxidizer solution gives almost as good results as an oxidizer solution containing formalin but its keeping quality is not as good as when formalin is used.

It is also possible to use, in this solution, furfuraldehyde or other equivalent aldehydes instead of acetaldehyde.

(12) Still another oxidizer solution consists of:

3% solution of bromine	oz	3
Formalin	drams	3 to 4
Hydrochloric or other equivalent acid	do	2 to 4
Distilled water	oz	3

I have also found that instead of an aldehyde I may use, with very good results, ketones as for instance acetone; the oxidizing qualities of a solution containing acetone instead of an aldehyde are very good. The only disadvantage is that such a solution does not keep as long as one containing an aldehyde.

I want to stress that for retouching purposes or for correcting the transparency of a photographic picture only without forming a screen thereon all of the above described oxidizers may be used without the addition of acid. In this case, however, the oxidizer is only adapted for immediate use and cannot be stored. By addition of the acid it may be made durable for practically unlimited time. The oxidizer may be used immediately after addition of the acid but I prefer to use it only about 5 to 7 days thereafter.

As set forth above, my oxidizer is adapted for correcting the transparency of the entire picture; this is of great importance in case of color transparencies. Due to various causes, a veil is formed even upon the most carefully exposed and properly processed color transparencies made by additive color processes. This veil prevents the transparencies from appearing to the observer in the natural colors and thereby falsifies the colors to a certain extent and gives the transparency a more or less flat and blurred appearance, especially if the transparency is slightly under- or over-exposed. The same veil can be found also on normal black and white or color separation pictures.

With my new oxidizer it is possible to eliminate this veil. The oxidizer is also adapted to work as a reducer if this is required and advisable.

It is not advisable to carry out the process of oxidation in clear daylight as the oxidizer loses activity in such light. The length of time for keeping the color transparency in the oxidizer

bath is generally from about 1 to 5 minutes, depending on the density of the transparency. I have found that by keeping the color transparency in the oxidizer bath, a grey tinge is formed on the surface of the transparency; this tinge disappears after the hypo treatment. In preparing the oxidizer bath it is necessary to add water only if the solution is used soon after it has been prepared. If it is about 1 or 2 weeks old usually no addition of water is necessary.

My oxidizer also may be used for a novel method of local color correction by oxidation which comprises the steps of coating the picture portions of the emulsion which are not to be corrected with a transparent resist, immersing the emulsion in an oxidizer bath of the type described, thereby correcting the uncoated parts of the picture and, after bathing the picture in a special hypo as described above, removing the resist from the emulsion. I want to note that I may cover the parts not to be treated with the oxidizer either by coating them with a resist in the usual manner or by applying the resist with an air brush; in the first case I will obtain a sharp outline between the treated and untreated image portions, while in the latter case I will obtain a soft merging edge portion between these image parts. In this way it is possible to correct picture parts of color transparencies. If it is desired to make one or the other color lighter, this can also be done by this process.

Using this process for color separation negatives, I can correct one or the other part of one of the negatives, thereby correcting the final picture attained after combination of the color separation negatives. For such color separation negatives it is preferable to use a solution which is at least a few weeks old and to use this solution without addition of water as this kind of negative needs a stronger treatment. The oxidizer solutions made with decolorized tincture of iodine N. F. IV are the most satisfactory for this purpose. The action of the oxidizer on glossy and on mat papers is different: if glossy paper prints are treated with the oxidizer, they remain absolutely clear during processing while mat paper prints are covered with a grey veil through the entire picture. This veil disappears in the hypo treatment.

As set forth above, it is also possible to obtain satisfactory results by treating photographic prints with my new oxidizer; it is specially adapted for treatment where it is necessary to regulate the contrast or softness of the prints produced in this way. The normal time of treatment is about 1 to 3 minutes, depending on the characteristics of the light sensitive paper used and on the density of the printed picture. For prints, it is advisable to use stock solutions which are a few weeks old and which contain salt or sugar, except when a solution containing nitric acid is used in which case no salt or sugar is to be added. It is not advisable to dilute this stock solution, or even fresh ones; in diluted state it will not be durable.

I may also use my oxidizer for retouching small parts of pictures, e. g. for removing or lightening dark spots, such as blemishes, freckles, wrinkles and the like on black and white and color separation pictures or on color transparencies.

If any of the oxidizer solutions described above were to be used for this local retouching, practically no result would be obtained as these solutions are too weak and work too slowly. I

therefore propose to use for this purpose an oxidizer solution comprising:

	Drams
Concentrated iodine or tincture of iodine U. S. P., alcohol 83%	1
Decolorized tincture of iodine N. F. IV	3
Formalin	1
Hydrochloric acid	1
Glycerine (to be added before using).	

The components of this solution have to be dissolved in glycerine before using the oxidizer. If the acid and formalin are omitted from this composition, this local oxidizer decomposes quickly and lasts only a short time, but if composed as above described it will keep indefinitely, even without addition of glycerine. The addition of glycerine greatly increases the life of the local oxidizer, even when kept in an open vessel ready for use.

This oxidizer is very effective and should be applied very gently as otherwise it may burn holes into the photographic material. It is not necessary to rub with the brush while applying the oxidizer, as every touch gives almost immediately a retouching result. Immediately after noticing that the applied local oxidizer has had the desired result the spot to which the oxidizer has been applied should be treated with a strong hypo. It is important to avoid touching other places with this hypo. After applying the hypo, the retouched photographic picture has to be washed thoroughly. I want to note that when larger areas are to be treated with my oxidizer for retouching purposes, it is advisable to cover this area first with a glycerine and water mixture and to carry out the retouching within this area thereafter.

The above description of my new oxidizers and of the processes for correcting the transparency of entire photographic pictures or local large areas, where resists are used, and for retouching small spots on photographic pictures by these oxidizers, shows clearly the advantages of these oxidizers and of the processes when compared with the means and methods known and used heretofore for these purposes. My new oxidizers are always ready for use, inexpensive in preparation, and adapted for all the purposes enumerated above.

As stated in the introductory part, the above described new oxidizers are advantageously used in combination with new resists described below in detail. In accordance with my present invention, these new resists consist of a composition of matter comprising a transparent substance selected from the group consisting of waxy and resinous substances dissolved in a transparent liquid solvent for said substance. This resist may be produced either as a quick-drying or as a non-drying resist. It may also be made as a transparent or as an opaque resist.

My quick-drying transparent resist comprises preferably Canada balsam and benzol. If it is to be applied in the usual way, I propose to dissolve one part by volume of Canada balsam in about 8 parts by volume of benzol or another solvent for said Canada balsam. If it has to be applied with an air brush, it is advisable to use a solution comprising one part Canada balsam dissolved in about 12 to 16 parts of benzol.

My non-drying transparent resist preferably comprises wax, lanoline, and white petrolatum. A preferred composition for this non-drying resist consists of:

	Grams
Wax, white or yellow, preferably white	1
Lanoline (wool fat)	2
White petrolatum	Between 12 and 15

If a non-drying opaque resist is desired, I can include in the above described non-drying transparent resist solution Indian red pigment or white lead carbonate or other substances making it opaque.

As a drying opaque resist, the following composition may be used:

	Ounces
Bees' wax	4
Oil of turpentine	8
Asphalt varnish (of Eimer and Amend make)	1
Red pigment	About 14
White lead carbonate	About 1

This opaque resist cannot be washed off with cold water; hot water, however, can be used for removing it.

I may use these resists for the most diverse purposes:

One of the principal purposes of my new resists is to cover a part of a picture during oxidation, thereby holding back the action of an oxidizer on this part while other parts are left uncovered and may be processed with the oxidizer in any desired way. My new resist in specially adapted for this process as it is transparent and thus it is possible to compare during processing the parts to be treated with the parts remaining untreated and thereby to regulate the timing of treatment as necessary. Another purpose of my resist consists in covering a part of a picture while the adjacent part is retouched, e. g. removed. Still another field in which my resist can be used is to cover pictures or paintings, retouched with an air brush, with it; if my transparent quick-drying resist is used, such a resist layer preserves the paint from being rubbed or washed off and adds a great deal to the brilliancy of the picture; furthermore, it preserves the paintings from cracking or discoloration. My new quick-drying resist may also be used for plates or films for natural color transparencies; in this case an extremely thin layer of quick-drying transparent resist has to be applied to the color screen under the light sensitive emulsion, making the color screen more transparent. My opaque quick-drying resist has substantially the properties of a transparent resist as described above.

My non-drying transparent resist has the property of resisting acids. It also remains in a non-drying condition while the photographic film or plate is being processed; this expedites the whole process as the resist can be easily and quickly applied and also easily and completely removed after processing, when the film or plate has dried and the resist is no longer needed. This non-drying transparent resist can be used also on prints to cover certain parts if it is desired to process other uncovered parts.

Having thus described in detail my new oxidizers and the resists to be used in combination with these oxidizers, and also the processes by which these oxidizers and resists are produced and the manner in which they may be used, I want to stress that numerous modifications and adaptations of the embodiments of my invention described above could be made without departing from the scope of my invention.

Without further analysis, the foregoing will so fully reveal the gist of this invention that others can by applying current knowledge readily adapt it for various applications without omitting certain features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention, and therefore such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the appended claims.

What I claim is:

1. As an oxidizer for the purposes of the character described, a solution comprising a halogen selected from the group consisting of iodine and bromine, an aldehyde, and an acid selected from the group consisting of hydrochloric, sulphuric, and nitric acids.

2. As an oxidizer for purposes of the character described, an aqueous solution of iodine, an aldehyde, and an acid selected from the group consisting of hydrochloric, sulphuric, and nitric acids.

3. As an oxidizer for purposes of the character described, an aqueous solution of formaldehyde, a halogen selected from the group consisting of iodine and bromine, and an acid selected from the group consisting of hydrochloric, sulphuric, and nitric acids.

4. As an oxidizer for purposes of the character described, an aqueous solution of iodine, formaldehyde, and an acid selected from the group consisting of hydrochloric, sulphuric, and nitric acids.

5. As an oxidizer for purposes of the character described, a composition of matter comprising iodine, sodium chloride, formaldehyde and an acid selected from the group consisting of hydrochloric, sulphuric, and nitric acids.

6. As an oxidizer for purposes of the character described, a composition of matter comprising iodine, sugar, an aldehyde, and an acid selected from the group of hydrochloric, sulphuric, and nitric acids.

7. As an oxidizer for purposes of the character described, a composition of matter comprising iodine, sugar, formaldehyde, and an acid selected from the group of hydrochloric, sulphuric, and nitric acids.

8. As an oxidizer, a composition of matter comprising a free halogen selected from the group consisting of iodine and bromine, an aldehyde, and an acid selected from the group consisting of hydrochloric, sulphuric, and nitric acids, said substances being intimately mixed with glycerine.

9. As an oxidizer, a composition of matter comprising iodine, formaldehyde, and an acid selected from the group consisting of hydrochloric, sulphuric, and nitric acids, said substances being mixed with glycerine.

10. As an oxidizer for purposes of the character described, an aqueous solution comprising iodine, decolorized iodine, formaldehyde, and an acid selected from the group consisting of hydrochloric, sulphuric, and nitric acids.

11. As an oxidizer for purposes of the character described, a composition of matter comprising iodine, decolorized iodine, sodium chloride, formaldehyde, and an acid selected from the group consisting of hydrochloric, sulphuric, and nitric acids.

12. As an oxidizer, a composition of matter comprising iodine, decolorized iodine, formaldehyde, and one acid selected from the class consisting of hydrochloric, sulphuric, and nitric acids, said substances being mixed with glycerine.

LEON RUBINSTEIN.

(References on following page)

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
641,919	Andresen et al.	Jan. 23, 1900
1,214,940	Miller	Feb. 6, 1917
1,992,169	Bruster	Feb. 26, 1935
2,206,572	Landis	July 2, 1940

FOREIGN PATENTS

Number	Country	Date
261,201	Great Britain	Nov. 18, 1926