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NONACID PHOTOGRAPHIC OXIDIZERS

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3 Claims. (Cl. 95-88)

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This invention relates to non-acid, photographic oxidizer-modifiers used for adjusting the image clarity and intensity, in whole or in part, including retouching, on the various types of photographic negatives, slides, and other transparencies, as well as on the many types of photographic prints. The invention includes also new and transparent resists for joint use with these oxidizers and others by being applied on the emulsion surface over those parts of it or of the image that are not to be acted on by the oxidizer.

The various non-acid oxidizer-modifiers of the invention are effective for clarifying, for example, by removing the haze or veil that gives a transparency a flat or blurred appearance, independently of, and especially if, it was overexposed or overdeveloped, and for retouching, photographic negatives, prints, and pictures of various types, for example, black and white, negatives as well as positives, such as X-ray plates, motion picture films, and especially color separation pictures and color transparencies, produced, for example, by additive color photographic processes, such as motion picture negatives, lantern slides and the like, as well as to adjust the tint of the yellow component of the subtractive color process.

This application is a continuation-in-part of my copending application Serial No. 642,981, filed January 23, 1946, and now Patent No. 2,467,357, issued April 12, 1949, which in turn is a continuation of my application Serial No. 453,671 (abandoned subsequent to the filing of my application Serial 642,981), filed August 5, 1942, and which in turn is a continuation-in-part of my application Serial No. 352,517, filed August 14, 1940, and abandoned subsequent to the filing of my application Serial No. 453,671.

Fundamentally the non-acid oxidizer-modifiers of the invention manifest their effectiveness for their various respective applications by containing at least one halogen accompanied by at least one water-soluble (or at least soluble in water having possibly up to about 5 to 10% or so of ethanol) aliphatic aldehyde or ketone, and more effectively lower aliphatic and having up to about 6 or 8 carbon atoms, whether open chain or cyclic, for example formaldehyde, acetaldehyde, furfuraldehyde (included as a lower cyclic aliphatic aldehyde), acetone, and the like. The aldehydes and ketones included are inert to the halogens in aqueous, acid aqueous, aqueous alcohol, and acid aqueous alcohol media. Among them the aldehydes are especially useful and of these formaldehyde is generally particularly distinctively effective.

The individual halogens show individual behavior dependent on the particular variations of compositions and conditions employed. Iodine

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and bromine for the most part are distinctively effective and of these iodine is more generally desired because of the more general employment of the iodide of silver in photosensitive films. Chlorine and fluorine manifest certain similarities in behavior, and of the two chlorine may be the more favored in use because of the more general commercial use of chlorine of the two of them.

The halogen and the aldehyde or ketone are used together as the principal ingredients of my non-acid oxidizer-modifiers most generally in an essentially aqueous vehicle. In the case of iodine, it is advantageous and preferable to effect the dissolution of the iodine in such vehicle, to use an alkali metal salt capable of taking iodine into aqueous solution, for example an alkali metal iodide such as potassium iodide or an alkali metal thiosulphate as sodium thiosulphate. Moreover, when I use a highly concentrated and advantageously saturated solution of iodine in alkali metal iodide-containing water, I can replace the aldehyde or ketone by one of the decolorized iodine solutions which usually contain iodine dissolved in water by the aid of an alkali metal iodide or thiosulfate with the addition of a little alcohol and decolorized by the inclusion of ammonia and diluted and stabilized with more alcohol, such as the tincture decolorized iodine, designated in the examples as "decolorized iodine N. F. IV" and included in "The National Formulary," third and fourth editions, published by J. B. Lippincott Company, Philadelphia, Pennsylvania, United States of America, and in others of the examples as "decolorized iodine N. F. VI," for the modification given in the fifth through eighth editions of the same publication.

My oxidizer-modifier of this invention, and which species I designate as the non-acid oxidizer-modifier because it does not contain any acid as a constituent, is effective for the various applications of adjusting the image clarity and intensity, in whole or in part, and including removal of the veil or haze, retouching, control of contrast and also of softness, and also clarifying half tone dot etching screen bearing images. A batch of non-acid oxidizer-modifier ordinarily will keep usually for about a working day's period, generally from several hours, say, six or seven, to two or three days or more depending on the individual composition. Although my non-acid oxidizer-modifiers are stable for very long and substantially unlimited periods when they are highly concentrated or saturated as to the halogen, e. g. iodine, content, as exemplified by taking a high concentration (up to saturation) of crystalline iodine into water solution by using preferably an aqueous potassium iodide solution

as solvent for the iodine, and then adding the aldehyde or ketone, such as formaldehyde.

In many of the illustrative examples there are included particular amounts of certain specifically individually designated iodine solutions, the detailed constitution and preparation of which follows:

(a) *Concentrated iodine*.—This is actually a saturated aqueous solution of iodine prepared, for example, by dissolving one ounce of crystalline potassium iodide in three liquid ounces of water and then adding more and more crystalline iodine until the solution is seen to be saturated with iodine as noted by the failure of any more of it to go into solution. After filtering off the excess or undissolved iodine, the concentrated (thus saturated) iodine solution is ready for use as an ingredient in the various oxidizer-modifier compositions.

(b) *Decolorized iodine N. F. VI* is prepared by addition to a solution of 25 grams of potassium iodide in 400 cc. of water of 50 grams of iodine and 400 cc. of alcohol and stirring. After the iodine is completely dissolved, 100 cc. of stronger ammonia water (about 37% NH_3) are added and the mixture allowed to stand until it becomes colorless. Thereafter sufficient alcohol is added to bring the volume to a total of 1000 cc.

(c) *Decolorized iodine N. F. IV*.—Digest 83 grams each of iodine and sodium thiosulphate in 100 cc. of water, at a gentle heat, until complete solution results. Then add 125 cc. of alcohol and afterwards 65 cc. of stronger ammonia water (37%). Shake the mixture a few minutes until bubbles of gas no longer escape, and the liquid has become colorless with a white precipitate suspended in it. Now cool the mixture, and then add sufficient alcohol to make the product measure 1000 cc. Place the bottle containing the liquid in a cold place for a few hours and then filter. Preserve in a well-stoppered bottle.

(d) *Tincture of iodine U. S. P.*—Dissolve 70 grams of potassium iodide in 50 cc. of distilled water contained in a bottle graduated to 1000 cc.; add 70 grams of iodine and agitate the mixture until solution is effected. Then add sufficient alcohol to make 1000 cc., and mix thoroughly.

(e) *Iodine test solution*.—Dissolve 1 gram of iodine and 3 grams of potassium iodide in 50 cc. of distilled water.

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

(g) *Lugol's solution iodine compound* is the standard U. S. Pharmacopoeia solution containing in each 100 cc. not less than 4.5 grams and not more than 5.5 grams of iodine and not less than 9.5 grams and not more than 10.5 grams of potassium iodide.

My non-acid oxidizer-modifiers are illustrated by, but not restricted to, the following examples:

- | | | |
|-------------------------------|----------|----|
| (1) Concentrated iodine | drams | 1 |
| Decolorized iodine N. F. VI | do | 3 |
| Formalin (40% HCHO) | do | 1 |
| Distilled water | liq. oz. | 16 |

This oxidizer presently most effective for substantially all of the above mentioned applications is prepared preferably by combining the concentrated iodine and the decolorized iodine, and then adding half of the water, the formalin and then adding the rest of the distilled water.

- | | | |
|----------------------------------|----------|----|
| (2) Concentrated iodine solution | drams | 1 |
| Decolorized iodine N. F. VI | do | 3 |
| Formalin | do | 3 |
| Distilled water | liq. oz. | 16 |

5 This oxidizer solution, most advantageously effective for clarifying extremely dense color transparencies where no white objects are visible, is preferably made by diluting the concentrated iodine with half of the water, separately combining the decolorized iodine and the formalin, and thereafter combining the two solutions. Then the second half of the water is added and the oxidizer is ready for use without filtering.

10 (3) For the present, I prefer the following oxidizer for clarifying detail in color transparencies:

- | | | |
|---|----------|-----|
| Tincture of iodine U. S. P. | drams | 3 |
| Decolorized tincture of iodine N. F. VI | drams | 3 |
| Formalin | do | 1-3 |
| Distilled water | liq. oz. | 16 |

20 This oxidizer is prepared, for example by placing the acid in a bottle and slowly, and cautiously where necessary, pouring into it half of the water, then combining this acid solution with the tincture of iodine, the decolorized iodine and the formalin, and thereafter adding the second half of the water. No filtering is necessary.

25 If it is desired to use this oxidizer-modifier on paper prints, two ounces of common salt or sugar should be added. This oxidizer is prepared, for example, by adding half of the water to the tincture of iodine, then the decolorized iodine and the formalin, and thereafter adding the second half of the water. No filtering is necessary.

30 (4) The following oxidizer-modifier can also be used for adjusting the clarity of color transparencies:

- | | | |
|---|----------|--------|
| Tincture of iodine U. S. P. | drams | 3 |
| Decolorized tincture of iodine N. F. VI | drams | 3 |
| Formalin | do | 1 to 3 |
| Distilled water | liq. oz. | 7 |

35 I prefer to make this solution by first combining the iodine with the formalin and then adding the water, and filtering.

- | | | |
|---|----------|--------|
| (5) Tincture of iodine U. S. P. | drams | 3 |
| Decolorized tincture of iodine N. F. IV | drams | 3 |
| Formalin | do | 1 to 3 |
| Distilled water | liq. oz. | 7 |

40 This oxidizer-modifier is prepared substantially similarly to that of example 4. Use of decolorized tincture of iodine N. F. IV makes the filtering step of Example 4 unnecessary.

45 (6) The following is a presently preferred oxidizer-modifier that is well adapted for developing softness on color transparencies and on prints:

- | | | |
|---|-------|--------|
| Iodine test solution U. S. P. | drams | 2 or 3 |
| Potassium iodide test solution U. S. P. | drams | 1 |
| Distilled water | oz. | 7 |

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

- | | | |
|---|----------|----|
| 70 Iodine test solution U. S. P. | drams | 1½ |
| Decolorized iodine N. F. IV | do | 1½ |
| Tincture of iodine U. S. P. (alcohol 83%) | drams | 2 |
| Formalin | do | 2 |
| 75 Distilled water | liq. oz. | 14 |

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Prepare this oxidizer by first diluting the iodine test solution with half of the water and in sequence add the decolorized iodine, the potassium iodine test solution, the tincture of iodine, and the formalin, and finally the rest of the water. This solution works very well but within about 6 to 10 days becomes decolorized and practically ineffective. By addition of sufficient of a strong iodine solution, for example, tincture of iodine or concentrated iodine it is revived to its former strength.

(8) Solution iodine compound (Lugol)
 U. S. P. _____ drams. 1
 Decolorized tincture of iodine N. F. _____
 VI _____ do. 2
 Formalin _____ do. 2
 Distilled water _____ liq. oz. 14

(9) Another useful solution consists of:

Churchill's tincture of iodine N. F. (alcohol 62%) _____ dram. ½
 Decolorized tincture of iodine N. F. IV _____ do. 1
 Formalin _____ do. 1
 Distilled water _____ liq. oz. 14

(10) An oxidizer-modifier that is much stronger than any of those in the preceding examples and especially adapted for half-tone dot etching is prepared by taking any of the oxidizer-modifier solutions of any of the preceding examples, in the amount of 8 oz. and adding the following:

Ounces
 Tincture of iodine U. S. P. _____ About 2½
 Formalin _____ About 2½

In place of tincture of iodine, 1 to 1¼ oz. of concentrated iodine can be used just as well. In all cases the quantities are in liquid measure.

While formaldehyde is included as the illustrative aldehyde in each of the preceding examples, it is understood that other suitable aldehydes can replace it in equivalent amounts, as exemplified by the following example:

(11) Concentrated iodine _____ drams. 3
 Acetaldehyde _____ do. 1 to 3
 Distilled water _____ liq. oz. 8 to 16

The concentrated iodine can be replaced by 6 drams of tincture of iodine U. S. P. or of any of the dilute iodine solutions such as any of the iodine test solutions, decolorized iodines, Churchill's tincture, or Lugol's tincture, and the like. A corresponding solution can be prepared with the equivalent amount of any other available effective aldehyde, such as furfuraldehyde, and the like. The oxidizer-modifiers made with aldehydes other than formaldehyde show activity relatively comparable with it in the various uses, but are somewhat under it as to duration in keeping qualities. The non-acid oxidizer-modifiers having acetaldehyde or furfuraldehyde are comparably as effective as the formaldehyde containing oxidizers in the various applications.

While iodine has been included in the preceding examples as the effective halogen, the various iodine solutions included in these examples can be replaced with equivalent amounts of the other halogens, however, in the form of aqueous solutions because of their greater solubility in water, for example:

(12) Bromine (as 3% aqueous solution) _____ liq. oz. 3
 Formalin _____ drams. 3 to 4
 Distilled water _____ liq. oz. 3

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Further exemplifying the non-acid oxidizer modifiers is:

(13) Chlorine (as 2½ to 5% aqueous solution) _____ liq. oz. 4
 Formalin _____ drams. 4
 Water to make a total of _____ liq. oz. 8

This composition can be used for adjusting the yellow color component of an image developed on Kodachrome film; although on such films it is preferable to use a weak solution, such as one that is already partly exhausted. This oxidizer composed with chlorine, or in its place a similar quantity of fluorine, in the same concentration aqueous solution, shows its effectiveness usually by attacking more strongly the silver in the darker parts of the image than do the compositions containing iodine. An example with fluorine is:

(14) Fluorine (as 3% aqueous solution) _____ liq. oz. 3
 Formalin _____ drams. 3 to 4
 Distilled water _____ liq. oz. 6 to 8

Other desirable illustrative, but not limiting, examples of the non-acid species of oxidizer-modifiers are:

(15) Concentrated iodine _____ drams. 3
 Formalin _____ do. 3
 Water _____ liq. oz. 10 to 12

This oxidizer, prepared by combining the iodine solution and water and adding the formalin, brings out strikingly well the contrasts in a picture by its effecting more of the lighter parts of the picture than the darker ones.

An oxidizer that makes a softer picture by its effecting the darker parts of it rather than the grey parts of the image, is illustrated by the following:

(16) Concentrated iodine _____ drams. 2 to 3
 Decolorized iodine N. F. IV or VI _____ do. 3
 Water _____ liq. oz. 10 to 12

This is prepared by mixing the water and the concentrated iodine and adding the decolorized iodine and shaking well. The inclusion of the decolorized iodine appears to operate to retard the characteristic fat-like spreading appearance ordinarily shown by concentrated iodine alone and thereby balances the oxidizer and makes it especially effective for paper prints.

The iodine in this last example can be replaced by equivalent amounts respectively of chlorine, bromine or fluorine, each separately in aqueous solution of it of the strength shown, for example, in Examples 12 and 13 respectively and with similar effectiveness.

While all of the preceding examples show some aldehyde as a particular constituent of my oxidizer-modifiers, for functioning in them, I believe, in some manner to control or restrain the activity of the halogen on the liberated silver in the image and thereby avoid any destruction of the details of it, I may use instead a ketone of the type hereinabove described, for example, in a composition of:

(17) Tincture of iodine U. S. P. _____ drams. 3
 Decolorized iodine N. F. VI _____ do. 3
 Acetone _____ do. 1 to 3
 Distilled water _____ liq. oz. 16

Such compositions containing a ketone show good

effectiveness in various of the indicated photographic applications.

Except when they are prepared from one of the concentrated iodine solutions, such as a saturated iodine solution or tincture of iodine U. S. P., the non-acid oxidizer-modifiers keep for only a short time, as noted above for from several hours to for the best part possibly two or three days, or perhaps slightly longer, depending on composition and conditions. It is usually undesirable to use my oxidizer-modifiers in clear daylight when adjusting photo images as they lose activity to a measure in such light.

The water constituent has been included as distilled water in the various preceding examples because it is most dependable. However, the recently made available demineralized water is adequately useful as well as any good quality tap water. Actually, the primary precaution is that the water should not have excessive silica and lime content.

The capacity of my non-acid oxidizer-modifiers for correcting the transparency of an entire picture is of considerable importance in color transparencies. It is well known that even with the most carefully exposed and processed color transparencies made by additive color processes, and just as occurs in ordinary black and white, or even in color separation, negatives and prints, there is formed a haze or veil that gives the transparency a more or less flat and blurred appearance, independently of whether, and especially if, it was slightly under or over-exposed, thereby preventing the transparencies from appearing to the observer in the natural colors. My oxidizer-modifiers eliminate this haze or veil, and equally as well from black and white transparencies and prints.

Generally a color transparency is kept in the oxidizer bath from about 1 to 5 minutes, depending on the density of the transparency. In the oxidizer bath, a grey tinge forms over the transparency, but disappears after the usual hypo treatment. The action is somewhat different on glossy and on mat papers. Glossy paper prints remain absolutely clear during processing while mat paper prints become covered overall with a green-grey and violet veil which disappears in the hypo treatment. The normal time of treatment is about 1 to 3 minutes, depending on the characteristics of the light sensitive paper used and the density of the printed picture. For prints, it is preferable to use one of the concentrated iodine containing non-acid type such as those of Examples 13, 14 and 15. This concentrated non-acid type keeps indefinitely.

My non-acid oxidizer-modifiers are also used for retouching small parts of pictures, such as for removing or lightening dark spots, such as blemishes, freckles, wrinkles and the like, for example, on black and white and color separation pictures or on color transparencies not quite completely satisfactory results are obtained if for such local retouching there is used any of my solutions of the various preceding examples as these work too slowly for this purpose. I therefore prefer to use for this purpose a strong oxidizer solution, which can be designated as a local oxidizer-modifier, illustrated by:

Drams

- | | |
|--|---|
| (18) Tincture of iodine U.S.P. (alcohol 83%) | 3 |
| Decolorized tincture of iodine N. F. IV | 3 |
| Formalin | 3 |
| Glycerine (to be added before using, preferably to a medium syrupy viscosity). | |

The tincture of iodine can be replaced by one-half dram of concentrated iodine. The other ingredients have to be dissolved in the glycerine before using this oxidizer-modifier. As above composed it will keep indefinitely without addition of glycerine, but addition of glycerine greatly increases its life, even when kept in an open vessel ready for use. This oxidizer is highly active and should be applied very gently for otherwise it may burn holes in the image being treated. It is unnecessary to rub with the brush while applying this oxidizer for each dab gives almost instantly a retouching result. Immediately after noting that the applied local oxidizer obtained the desired result, the spot to which it was applied should be treated with a strong hypo. It is important to avoid touching other places with the hypo. After applying the hypo, the retouched film or color transparency has to be washed thoroughly. When larger areas are to be treated with this oxidizer for retouching purposes, it is advisable first to cover such area with a glycerine and water solution (medium syrupy viscosity) and thereafter to do the retouching within that area. The function of the glycerine here and in the oxidizer is to protect the edges of the film, and especially of the paper print (due to the greater absorbability of the paper), and also in local retouching to avoid leaving a sharp outline about the retouched area, due to the high activity of such stronger oxidizer-modifier.

My non-acid oxidizer-modifiers are specially adapted for treating photographic prints where it is necessary to adjust their contrast or softness. In removing the haze or veil from an image, my oxidizer-modifiers in essence serve as a photographic reducer (not to be confused with the same word in its strict chemical parlance).

My non-acid oxidizer-modifiers in general are easily prepared for use, inexpensive, and effectively adapted for the various purposes enumerated above. Their use on transparencies bearing also an image of a half-tone dot etching screen, as more fully discussed hereinbelow, greatly simplifies that process, makes it easier to control and yields much better results than by other known methods.

My non-acid oxidizer-modifiers can be used also for a novel method of local color correction by oxidation. This includes the steps of coating with my new and transparent resists the picture portions of the emulsion, which are not to be corrected, immersing the emulsion in one of my oxidizer baths for a sufficient time for the correcting action on the uncoated parts of the picture, and, after bathing the picture in a special hypo described below, removing the resist from the emulsion. The parts not to be treated with the oxidizer can be coated with my new resists either in the usual manner or by application with an air brush. By the usual method, there occurs a sharp outline between the treated and untreated image portions, while with an air brush a soft merging edge portion between these image parts is obtained. Thus, it is possible to correct picture parts of color transparencies, even also, if desired, to make one or the other color lighter or brighter.

By this process I can correct also one or the other part of any one of the color separation negatives, and thereby correct the final color transparency obtained after combining them. The oxidizer-modifiers made with decolorized

tincture of iodine N.F. IV are the most satisfactory for this purpose.

Accordingly, my new non-acid oxidizer-modifiers are advantageously used in combination with my new resists which are compositions of matter comprising a transparent substance inert to gelatin and selected from the group consisting of transparent waxy and resinous substances and dissolved in a transparent liquid solvent for said substances and which is inert to, and not a solvent for, gelatin; for example, preferably Canada balsam as the solute and benzol as the solvent. They can be produced either in a quick-drying or in a non-drying type.

If the resist is to be applied in the usual way, then I prepare it by dissolving one part by volume of Canada balsam in about 8 parts by volume of benzol or other solvent for the Canada balsam. If it is to be applied with an air brush, then it is advisable to use a solution comprising one part by volume Canada balsam dissolved in about 12 to 16 parts of benzol by volume.

My non-drying transparent resist advantageously comprises beeswax, lanolin, and white petrolatum, a preferred composition for it consisting of:

(19) Beeswax, white or yellow, preferably white	1
Lanolin (wool fat)	2
White petrolatum	Between 12 and 15

In this type no solvent is used. Other suitable examples are any two of the foregoing three ingredients combined together.

I can include certain additional ingredients to make a non-drying, opaque resist if desired. For this, I include in the above described non-drying transparent resist compositions, Indian red pigment or white lead carbonate or other compatible substances.

As a drying, opaque resist, the following composition can be used (by weight):

(20) Beeswax	4
Oil of turpentine	8
Asphalt varnish (e. g. Elmer and Amend make)	1
Red pigment	About 14
White lead carbonate	About 1

This opaque resist cannot be washed off with cold water, but hot water will remove it.

These resists are used for the most diverse purposes. One of the principal purposes is, as already illustrated, to cover a part of a picture during retouching and thereby withhold action of the oxidizer on such part while the uncovered other parts are processed with the oxidizer in any desired way. My new resists are especially adapted for such process for their transparency makes it possible during processing to compare the parts to be treated with those remaining untreated and thereby to regulate the time of treatment as necessary.

Another use of my resists is in the covering of a part of a picture while the adjacent part is removed. Still another field of use for my non-drying, transparent resist is to cover with them parts of pictures or paintings, retouched with an air brush. If my transparent, quick-drying resist is used, a layer of it preserves the paint from being rubbed or washed off and enhances considerably the brilliancy of the picture; and in addition preserves the paintings from cracking or discoloration. My new quick-drying resists 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. Except for its opacity, my opaque, quick-drying resists have substantially the same properties of my transparent resists as described above.

My non-drying, transparent resists are inert to acids and remain in a non-drying condition while the photographic film or plate is being processed, thus expediting the whole process as the resist can be easily and quickly applied and also easily and completely removed after the film or plate has been dried and the resist is no longer needed. This non-drying transparent resist can be used similarly also on prints.

My copending application Serial No. 642,981 describes and claims my acid species of oxidizer-modifiers. By developing this acid species, I found that I can fortify the oxidizer-modifier so that it will be otherwise generally stable and storable for a substantially unlimited time and in addition enhance its activity in adjusting image clarity and intensity and in retouching. I accomplished this by including in the halogen-aldehyde composition a suitable quantity of an acid, distinctively effectively a mineral acid of the type of hydrochloric, sulphuric, sulphurous, nitrosulphuric, nitric, and phosphoric acids, or other hydrohalogen acid as hydrobromic or hydroiodic acid or also hydrofluoric acid so long as the proper vessels are used along with precautions for safety in handling, or oxygen derivatives of the hydrohalogen acids such as the perhalo acids as perchloric or periodic acid and the like, or sulphamic acid as another example of a sulphur acid, or an organic acid advantageously aliphatic, and preferably lower aliphatic and of necessity soluble in water or water containing possibly up to about 5 to 10% or so of alcohol, for example, formic, acetic, lactic acid, and the like. I designate the oxidizer-modifier containing an acid as an acid oxidizer-modifier.

Moreover, in situations where a strong oxidizer is needed in local retouching use, it is advantageous to dissolve the halogen, for example iodine, and the aldehyde such as formaldehyde, along with the selected acid in glycerine or other hygroscopic polyhydric alcohol. The effect of such hygroscopic substance as the vehicle for solution of the usual ingredients of my acid oxidizer-modifiers is to safeguard the edges of the film and especially of the paper print due to the greater absorbability of the paper, and also in local retouching to avoid leaving a sharp outline about the retouched area, against any overactivity of such stronger oxidizer composition.

My acid oxidizer-modifiers are exemplified by adding to the composition of each of the above Examples 1 through 12, 17 and 18 hydrochloric acid 37% strength (or sulphuric acid 96-98% strength or nitric acid 70% strength) to the extent of 1 dram in each of Examples 1, 4, 5, 6, 7, 9 and 18, 2 drams in Examples 2, 3, 8 and 17, about two and one-half liquid ounces in Example 10, 1 to 2 drams in Example 11 and 2 to 4 drams in Example 12.

I can also influence the softness or the contrast in retouching images with either my non-acid or acid oxidizer-modifiers by including varying amounts of either sugar or common salt (NaCl) or of both as additional ingredients. This is exemplified by adding 2 ounces (by weight) of sugar or salt to the acidified compositions of Examples 1 and 2 as just above described and 1

ounce in Example 9. In these examples, I find it advantageous to add the acid to half of the water, then to add the combined iodine constituents, then the salt or sugar and to shake to whichever of the latter that is added is dissolved and then to add the balance of the water. Moreover, when nitric acid is used no sugar is added.

While in each of the preceding examples hydrochloric acid (and alternately sulphuric acid or nitric acid) was included as the acid constituent of the acid oxidizer-modifiers (respectively of the same strengths as shown in Example 1) with the caution not to use nitric acid in any formula that includes salt (and vice versa), any of the other acids compatible with the other constituents of the modifier-oxidizer and the film or print to be treated, can be used in equivalent amounts, such as any acid of the type described above. Those including hydrobromic, periodic, perchloric or sulphurous acid do not have quite the extent of life as do the preparations containing any of the other acids. As already indicated, ordinarily the acid constituent in my acid oxidizer-modifier serves to increase the rate of activity of the agent.

In addition to their utility in the various kinds of photography retouching operations described in the prior portions of this specification, my acid species of oxidizer-modifiers play an important role in the formation of several surprisingly useful types of transmitted-light-modifying screens that provide certain unusually effective optical phenomena. My non-acid oxidizer-modifiers are not suitable for making these screens. For use in making screens, it is preferable that distilled water be used in the acid-aldehyde agent.

While the invention has been illustrated by

describing certain specific embodiments of it, it is understood that suitable substitution of equivalents, modifications and variations may be made in them without departing from the spirit of the invention, the scope of which is recited in the appending claims.

I claim:

1. A non-acid, photographic oxidizer-modifier for adjusting the clarity of, and retouching, developed photographs, negative as well as positive, which comprises an aqueous solution of concentrated iodine, decolorized iodine, and a lower aliphatic water-soluble aldehyde.

2. A non-acid, photographic oxidizer-modifier as claimed in claim 1, wherein the aldehyde is formaldehyde.

3. A non-acid, photographic oxidizer-modifier as claimed in claim 1, wherein the concentrated iodine, decolorized iodine, and aldehyde are present respectively in amounts equivalent to about tincture of iodine U. S. P. 3 drams, about 3 drams decolorized tincture of iodine N. F. VI, and from about 1 to about 3 drams of formalin, and which oxidizer-modifier also contains about 16 liquid ounces of water.

LEON RUBINSTEIN.

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