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UNITED STATES PATENT OFFICE.

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PHOTOGRAPHIC DEVELOPER.

Original application filed December 18, 1918, Serial No. 267,409 Divided and this application filed August 10, 1921. Serial No. 491,296.

To all whom it may concern:

Be it known that I, NATHAN SULZBERGER, a citizen of the United States, residing at Hotel Netherland, New York city, in the county of New York, State of New York, have invented certain new and useful Improvements in Photographic Developers; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

The present invention relates to improved photographic developers of a stable character containing an aromatic hydroxyl-amin substance, and more particularly a salt of phenyl-hydroxyl-amin or its homologues or derivatives, etc., with an organic acid.

Beta-phenyl-hydroxyl-amin itself and certain of its derivatives are unstable in solution and particularly in alkaline solution, and even in a dry state, and, without special treatment, are not available for use as photographic developers.

The present invention relates to photographic developers which are relatively stable in character. The new photographic developers contain or are made from salts of the hydroxyl-amins and more particularly salts with organic acids.

When a relatively concentrated solution of phenyl-hydroxyl-amin in water is treated with a solution of oxalic acid (say about 10%) there is produced almost instantly a crystalline precipitate which is of stable character and which is also not very soluble in water. Under proper conditions a relatively pure precipitate can be obtained merely by filtering and washing. The resulting product I consider to be the oxalate (i. e., a salt of an organic acid) of the phenyl-hydroxyl-amin. It can be further purified and is stable in the air and can be kept for long periods of time.

Instead of combining the phenyl-hydroxyl-amin with oxalic acid it can be combined with other organic acids such as citric, formic lactic, pyrogallic, tannic, etc., or in general with such acids which have no detrimental action when combined with the phenyl-hydroxyl-amin, that is, no action detrimental for use as photographic developers. The acids employed should not of course be of such a character that the action of the developer will be destroyed or detrimentally influenced to an objectionable extent; acids enhancing the developing qualities are of particular value.

The new photographic developers contain the hydroxyl-amin substance with other suitable ingredients, including, if desired, also such as will tend to prevent or retard any too rapid or objectionable oxidation of the hydroxyl-amin substance itself, particularly in the alkaline solution.

I have found the following compositions well adapted for use for photographic developing purposes:

For a paper developer dissolve in 100 ounces of water—

Sodium sulfite (dry)	5-¼	ounces.
Hydroquinone	1	ounce.
Phenyl-hydroxyl-amin oxalate (as above described)	½	ounce.
Sodium carbonate (anhydrous)	10	ounces.
Potassium bromide (crystalline	6	grains.

In using this solution it can be diluted with water to the desired extent, and the paper to be developed may then be treated therewith in a manner such as is customary in the employment of developing solutions.

For developing films I have found the following formula of advantage:

Water	10	ounces.
Sodium sulfite (dry)	20	grains.
Hydroquinone	40	grains.
Phenyl-hydroxyl-amin oxalate- (as above described)	20	grains.
Sodium carbonate (anhydrous)	600	grains.
Potasium bromide (crystalline)	4	grains.

In using this developer it can be diluted with water to the desired extent, and may

then be used for developing films in much the usual manner, but with added advantage to the developing process and to the result produced.

Modifications of these formulæ as to quantity and nature of the added ingredients to meet various conditions for which the developer is to be used are to be considered as within the scope of the invention. Such additions may be for modifying the tone or increasing or retarding the action of the developer, etc.

Instead of the salts of phenyl-hydroxyl-amin itself with organic acids, other suitable compounds or salts of its homologues or of other aromatic hydroxyl-amins, such as naphtyl-hydroxyl-amin, etc., and their derivatives may be employed.

When using solid salts of the character described which are relatively stable, these salts can be kept for considerable periods of time and used in a dry state when desired, or they can be combined with other dry ingredients of the developer and the composite developer then added to water, or to other solution for use. The developer may thus be put up in tablet form, etc., either pure or mixed.

From the above formulae it will be noted that the phenyl-hydroxyl-amin oxalate is compounded with sodium sulfite and sodium carbonate as well as with other developer ingredients, for example, hydroquinone and potassium bromide. The sodium sulfite contributes to the developer composition and also has a protective influence upon the alkaline solution of the hydroxyl-amin substances. Other substances having similar action may be employed.

Variations and modifications can be made in the photographic developer without departing from the invention. For example, other phenyl-hydroxyl-amin compounds and derivatives may be similarly used as well as other photographic developer ingredients such as would be considered by those skilled in the art of value or as equivalents of those mentioned.

I do not claim herein the new salts of aromatic hydroxyl-amins with organic acids as these form the subject of my prior application, Serial No. 267,409, filed December 18, 1918, which matured into Patent No. 1,390,260, dated Sept. 6, 1921, of which this application is a division.

I claim:

1. A photographic developer containing an organic acid salt of an aromatic hydoxyl-amin together with other developer ingredients.

2. A photographic developer containing an organic acid salt of phenyl-hydroxyl-amin together with other developer ingredients.

3. A photographer developer containing an organic acid salt of an aromatic hydroxyl-amin together with sodium sulfite and other developer ingredients.

4. A photographic developer containing an organic acid salt of phenyl-hydroxyl-amin together with sodium sulfite and other developer ingredients.

5. A photographic developer containing phenyl-hydroxyl-amin oxalate together with other developer ingredients.

6. A photographic developer comprising an alkaline solution containing an organic acid salt of an aromatic hydroxyl-amin, and sodium sulfite.

7. A photographic developer comprising an alkaline solution containing an organic acid salt of phenyl-hydroxyl-amin and sodium sulfite.

8. A photographic developer comprising an aqueous solution of phenyl-hydroxyl-amin oxalate, together with sodium sulfite and sodium carbonate.

9. A photographic developer containing phenyl-hydroxyl-amin oxalate together with sodium sulfite.

10. A photographic developer comprising a solution in water of phenyl-hydroxyl-amin oxalate sodium sulfite, sodium carbonate, and hydroquinone.

11. A photographic developer comprising a solution in water of phenyl-hydroxyl-amin, oxalate sodium sulfite, sodium carbonate, potassium bromide, and hydroquinone.

12. A photographic developer containing in a dry state a stable aromatic hydroxyl-amin compound.

13. A photographic developer containing in a dry state a stable aromatic hydroxyl-amin compound together with sodium sulfite.

14. A photographic developer containing in a dry state a stable aromatic hydroxyl-amin compound together with sodium sulfite and hydro-quinone.

15. A photographic developer comprising a stable aqueous solution of an aromatic hydroxyl-amin compound together with sodium sulfite, hydro-quinone and sodium carbonate.

16. A photographic developer comprising a stable aqueous solution of an aromatic hydroxyl-amin compound together with a protective ingredient preventing objectionable too rapid oxidation of such compound.

17. The process of developing photograpic materials, which comprises treating the same with a solution of an organic acid salt of an aromatic hydroxyl-amin containing sodium sulfite and alkali.

18. The process of developing photographic materials, which comprises treating the same with a solution of phenyl-hydroxyl-amin oxalate containing sodium sulfite and sodium carbonate.

19. The process of developing photo-

graphic materials, which comprises treating the same with a stable solution of an aromatic hydroxyl-amin susbstance containing sodium sulfite, sodium carbonate and hydroquinone.

20. The process of developing photographic materials, which comprises treating same with a solution of phenyl-hydroxyl-amin oxalate containing also sodium sulfite hydroquinone and sodium carbonate.

21. The process of developing photographic materials, which comprises treating same with a solution of phenyl-hydroxyl-amin oxalate containing also sodium sulfite, hydroquinone, sodium carbonate, and potassium bromide.

In testimony whereof I affix my signature.

NATHAN SULZBERGER.