UNITED STATES PATENT OFFICE.

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DEVELOPMENT OF PHOTOGRAPHIC IMAGES.

1,082,622. Specification of Letters Patent. Patented Dec. 30, 1913.

No Drawing. Application filed June 19, 1912. Serial No. 704,623.

To all whom it may concern:

Be it known that I, WILLIAM HAY CALDWELL, a subject of the King of Great Britain and Ireland, residing in Invernessshire, Scotland, have invented Improvements in or Relating to the Development of Photographic Images, of which the following is a specification.

In the development of exposed silver haloid films there are three main factors to be taken into consideration, namely (*a*) the amount of the silver haloid in the film that has been affected by light, that is to say the number of unit portions of the haloid that have been affected; (*b*) the amount and nature of the reducer present in the developer and (*c*) the amount of silver haloid solvent present in the developer.

With all ordinary developers for bromid fast plates, the reducer is such that all dissolved silver bromid present in instantaneously reduced to silver in contact with altered silver salt produced by exposure to light with the result that the whole of the light affected unit portions of silver haloid on each grain of the silver haloid present in the film are not utilized in bringing about the reduction of the whole grain, one unit alone being sufficient to bring about the reduction of the whole grain so that the image is not developed in the most perfect manner desirable, especially in the case of over-exposed films. With such developers, therefore, the effective working units are the light affected aggregates of silver haloid, and since the effective working units are, compared to the number of molecules present, few in number, the "latitude" of the plate, as regards "exposure," is small. This action is independent of the changes due to exposure in the film as is shown by the fact that the films forming the subject matter of former Letters Patent granted to me No. 956,567 dated May 3, 1910, though incapable of injury through being over exposed, yet, with ordinary developers, cannot be developed to the same scale of gradations with different exposures.

Now the present invention has for its object to develop exposed photographic films with a developer such that the silver haloid, for example silver bromid, dissolved by the developer, shall not be reduced so quickly as in an ordinary developer but shall, on the contrary, have time to travel to all the unit portions of silver haloid that have been affected by light so that silver haloid in solution shall be reduced to silver in contact with each of the unit portions, whereby a perfect development of the photographic image can be obtained in the case of films that have had a long exposure. For this purpose I have found that very satisfactory results can be obtained by developing an exposed film with a solution of a double salt obtained by combining an aromatic hydrazin base and an alkali metal sulfite, or by using, though not with such good results, the sulfurous acid salt of the base itself. By these means, the proper function of a perfect developer is fulfilled, namely that the developer should reduce the silver salt in solution only when it is in contact with the light affected product and that the solution in the developer of the unaltered silver salt in the plate or film should be able to diffuse in the film without being reduced. Such a developer can be obtained by mixing, in molecular proportions, in one instance, a hydrazin base, for example phenyl hydrazin, with a solution of an acid sulfite of an alkali, for example acid sulfite of sodium, to produce

$$C_6H_5NH—NH_2NaHSO_3.$$

In all cases it is essential that the solution be acid to litmus. Even a slight excess of any alkaline salt, *e. g.*, Na_2SO_3, is sufficient to destroy the required property of the developer. The developer can also be prepared in the form of a dry white powder by mixing the hydrazin base with sodium bisulfite in equal molecular proportions and adding thereto water in the proportion of $3\frac{1}{2}$ molecules.

In practice it is found that phenyl hydrazin is irritating to the hands of the operator. By replacing one or more of the atoms of hydrogen in the para or ortho position in the phenyl nucleus with one or another of numerous available groups or certain elements this disadvantage is found to be overcome. Among suitable inorganic elements or groups may be mentioned chlorin, bromin or HSO_3 each possessing positive properties, or NH_2 possessing negative properties while a large number of organic groups or radicals as for instance hydrocarbon radicals such as methyl (CH_3), ethyl-

(C_2H_5) and so on are suitable. Substances of this character are included in the generic substitution bodies referred to in certain of the claims under the expression "anti-corrosive".

By the use of a developer such as described, the silver salt in the film is dissolved, transferred across the gelatin or like medium constituting the film and deposited on the whole of the separate light affected units present, the amount of silver reduced and deposited, and hence the density of the image obtained, being limited only by the amount of silver present in the film. On the other hand, in the case of an ordinary developer, the amount of silver deposited is limited by the amount of silver reduced by a given exposure and is dependent upon the number of grains of silver haloid affected.

By regulating the strength of the new developer by using more or less water, any desired gradation of the developed image can be obtained by well known laws, because, by altering the quantity of the solvent of the unaltered silver salts, one can vary the rate of solution compared to that of diffusion in the film. Thus, one can starve the high lights and produce a flat result by using more water and vice versa. Further control can be obtained by varying the temperature of the developer before use, as this changes the activity of the reducer in the developer.

A suitable stock developing solution can be prepared by dissolving one ounce of the new developer in the dry state in thirty three ounces of water at a temperature of 120° to 150° F., allowing the solution to cool and filtering it. For developing a film having an over-exposure of 10 to 100 times that technically called "correct", a suitable developer can be made by mixing two parts of the stock solution with one part of water and using the resulting developer at from 70° F. to 65° F., the average time of development being from 20 to 45 minutes. For developing a film having an exposure of from 100 to 1000 times, the stock solution can be used without further dilution, at a temperature of from 60° F. to 50° F., the rule being the longer the exposure the colder should be the developer. This rate will apply also to abnormal over exposures of say 5000 times and upward, where the temperature of the developer may be lowered to 35° F. These extreme over exposures can be developed at a higher temperature by the addition of solution to the developer solution.

The films before development may advantageously be immersed in a 2% solution of sodium carbonate (anhydrous) for about two minutes, then rinsed in water and the surface wiped with a pad of cotton wool.

The present invention can advantageously be applied in the development of images on photographic films or surfaces of the kind forming the subject matter of my said former Letters Patent No. 956567. With these films, any exposure however prolonged, up to complete "printing out", can be developed to give the correct scale of density.

What I claim is:—

1. The herein described improvement in the art of developing a photographic film containing a silver salt, which consists in subjecting the film to a slowly acting developer, acid to litmus, dissolving out thereby silver salt that has been unacted upon by light and causing the dissolved silver salt to slowly diffuse or travel through the film medium to all the unit portions of the silver salt that have been affected by light so that silver salt in solution shall be reduced to silver in contact with each of said unit portions, substantially as described for the purpose set forth.

2. The herein described improvement in the art of developing a photographic film containing a silver salt, which consists in subjecting the film to the action of a solution, acid to litmus, obtained by combining an aromatic hydrazin base with a compound containing sulfurous acid.

3. The herein described improvement in the art of developing a photographic film containing a silver salt, which consists in subjecting the film to the action of a solution, acid to litmus, of a double salt obtained by combining an aromatic hydrazin base and an alkali metal sulfite.

4. The herein described improvement in the art of developing a photographic film containing a silver salt, which consists in subjecting the film to the action of a solution, acid to litmus, of a double salt obtained by combining an aromatic hydrazin base and acid sulfite of sodium.

5. The herein described improvement in the art of developing a photographic film containing a silver salt, which consists in subjecting the film to the action of a solution, acid to litmus, of a double salt obtained by combining a phenyl hydrazin base and an alkali metal sulfite.

6. The herein described improvement in the art of developing a photographic film containing a silver salt, which consists in subjecting the film to the action of a solution, acid to litmus, of a double salt obtained by combining a phenyl hydrazin base in which an atom of hydrogen in the phenyl nucleus distant an odd number of positions from the hydrazin has been replaced by an anti-corrosive substance, with an alkali metal sulfite, substantially as described.

7. The herein described improvement in the art of developing a photographic film containing a silver salt, which consists in subjecting the film to the action of a solution, acid to litmus, of a double salt obtained by combining a phenyl hydrazin base in

which an atom of hydrogen in the phenyl nucleus has been replaced by a halogen, with an alkali metal sulfite.

8. The herein described improvement in the art of developing a photographic film containing a silver salt, which consists in subjecting the film to the action of a solution, acid to litmus, of a double salt obtained by combining a phenyl hydrazin base in which an atom of hydrogen in the ortho position in the phenyl nucleus has been replaced by an anti-corrosive substance, with an alkali metal sulfite.

9. The herein described improvement in the art of developing a photographic film containing a silver salt, which consists in subjecting the film to the action of a solution, acid to litmus, of a double salt obtained by combining a phenyl hydrazin base in which an atom of hydrogen in the phenyl nucleus distant an odd number of positions from the hydrazin has been replaced by bromin, with an alkali metal sulfite.

10. The herein described improvement in the art of developing a photographic film containing a silver salt, which consists in subjecting the film to the action of a solution, acid to litmus, of a double salt obtained by combining ortho-brom-phenyl-hydrazin with an alkali metal sulfite.

11. The herein described improvement in the art of developing a photographic film containing a silver salt, which consists in subjecting the film to the action of a solution, acid to litmus, of a double salt obtained by combining ortho-brom-phenyl-hydrazin with acid sulfite of sodium.

12. For developing photographic films containing a silver salt, a developer comprising an aromatic hydrazin base and an acid sulfite of an alkali metal.

13. For developing photographic films containing a silver salt, a developer comprising a phenyl hydrazin base in which an atom of hydrogen in the phenyl nucleus distant an odd number of positions from the hydrazin, has been replaced by an anti-corrosive substance, and an acid sulfite of an alkali metal.

14. For developing photographic films containing a silver salt, a developer comprising ortho-brom-phenyl-hydrazin and an acid sulfite of an alkali metal.

15. For developing photographic films containing a silver salt, a liquid developer comprising an aqueous solution, acid to litmus, of a hydrazin base and an acid sulfite of an alkali metal in equal molecular proportions.

16. For developing photographic films containing a silver salt a solution comprising a substitution product, in the phenyl nucleus, of phenyl hydrazin, said solution being acid to litmus and non-irritant to the skin.

Signed at Fort William, Invernesshire, Scotland, this sixth day of June 1912.

WILLIAM HAY CALDWELL.

Witnesses:

ALEXANDER MACKINTOSH,
ARCHIBALD W. McDONALD.