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UNITED STATES PATENT OFFICE.

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SELECTIVE PHOTOGRAPHIC HARDENING.

No Drawing.

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To all whom it may concern:

Be it known that LEONARD T. TROLAND, a citizen of the United States, and resident of Malden, in the county of Middlesex and State of Massachusetts, has invented new and useful Improvements in Selective Photographic Hardening, of which the following is a specification.

This invention relates to the selective treatment of the exposed and unexposed portions of light-sensitive films by which one of the portions, for example the exposed portion, is made harder than the other portion, whereby the two portions react differently to subsequent treatment, as for example a hot water etch in which the relatively soft portion is dissolved off leaving the other portion in relief or a dye bath in which the dye is absorbed predominately by one portion.

It has been proposed to effect this selective hardening in the developing process by employing a pyro developer comprising pyrogalllic acid and an accelerator such as sodium hydroxide or ammonium hydroxide. However, such developers have proved unsatisfactory, particularly in the production of motion picture film where a high degree of perfection and uniformity is required, owing to their inherent tendencies to harden the unexposed as well as the exposed portions, to vary from time to time in their action, to leave the exposed portions more or less friable, to produce chemical fog, etc. For example, the principal objection to a developer containing sodium hydroxide is its strong tendency to harden the unexposed as well as the exposed portions of the film; and the chief objection to the use of ammonium hydroxide, particularly in developing motion picture film, is the difficulty of securing uniform results in successive mixtures, this being largely due to the strong tendency of ammonium hydroxide to lose strength by evaporation when in the concentrated condition in which it is kept prior to mixing with the developer.

Objects of the invention are to provide a film treating composition and method by which the aforesaid selective hardening may be effected throughout long series of images with uniformity, to restrict the hardening to one of the aforesaid portions of the film, to make the hardened portion of the film firmer and less friable, to reduce the chemi-

cal fogging action of the composition, to increase the speed of action of the composition without substantially affecting the quality of the action, and to produce relief images which are more sharply etched and which are less likely to become scratched or otherwise mutilated in production or in subsequent use.

According to the present invention the developer and/or hardening composition is prepared by mixing with a developer and/or hardener such as pyrogalllic acid or other suitable polyhydroxybenzene, a fixed alkali accelerator such as sodium hydroxide and a salt of a relatively weak alkali, such as ammonium chloride or bromide or other halide.

The admixture of the salt of a weak base eliminates the objectionable effects of the fixed alkali accelerator which have heretofore rendered its use unsatisfactory. Instead of hardening the light-sensitive film more or less throughout, as pyro developers containing fixed alkali accelerators have heretofore done unless employed with a restrainer such as sodium sulphite, the fixed alkali and alkali halide product is notably free from this tendency. Moreover, in making relief images by etching off the unexposed portion of the film, the soft and delicate nature of the reliefs made with a hardener containing sulphite is avoided with this developer which yields exceptionally firm reliefs; and the reliefs are much more sharply defined, especially in machine operation, than reliefs produced by an ordinary pyro-ammonia developer.

A small amount of citric acid may be incorporated in the pyro stock solution for its preservative action on the solution before the developer is mixed. As is customary, potassium bromide may be added to the mixture to restrain fog, but as above stated one of the advantages of the fixed alkali and halide of a weak base combination is that it has this function. A satisfactory formula for use in developing and hardening motion picture film in a continuous machine is as follows: pyrogalllic acid .82 gms., citric acid, .02 gms., potassium bromide .40 gms., sodium hydroxide .34 gms., ammonium chloride .17 gms., and enough water to make a total of 100 c. c.

The sodium hydroxide and ammonium chloride react to some extent to form sodium chloride and ammonium hydroxide;

and better results seem to be attained by separately adding the sodium hydroxide and ammonium chloride just before use. The preferred method of mixing is to mix
5 the pyro in water, then mix in the chloride, and then add the sodium hydroxide.

To make relief positives with positive stock having therein a yellow dye as disclosed in the applications of Eastman A. Weaver Serial No. 512,390 and Serial No. 512,391, filed November 2, 1921, the development should be carried on for about two minutes at a temperature of 65° F. and the temperature of the etch water should be
15 about 130° F.

This developer has the desirable characteristics of both the well-known pyro-soda and pyro-ammonia developers without the undesirable characteristics of either. It has
20 the uniformity and reliability of pyro-soda, and the selectivity in hardening of pyro-ammonia; at the same time it produces less chemical fog than pyro-ammonia so that the developer may be made stronger and
25 the development more complete, and it does not tend to harden the unexposed portions of the emulsion as does pyro-soda. Moreover, this developer seems to be unique in that it produces firmer, sharper, less delicate
30 and less friable reliefs.

This developer eliminates the use of a restrainer such as sodium sulphite which is easily oxidized and unreliable in action and which has a softening effect upon the reliefs, making all the gelatine spongy. The
35 probable explanation of this marked difference in results is that the sulphite developer restrains the hardening action throughout both the exposed and unexposed portions
40 whereas the developer herein claimed avoids any tendency to harden in the unexposed portion inasmuch as it avoids chemical fogging.

What I claim:

45 1. A composition for treating light-sensitive film having exposed and unexposed portions which is constituted essentially of a hardener for hardening one of said portions, a fixed alkali accelerator and a salt of a
50 weak base.

2. A composition for treating light-sensitive film having exposed and unexposed portions which is constituted essentially of a developer adapted to harden one of said
55 portions, a fixed alkali accelerator, and a halide of a weak base.

3. A composition for treating light-sensitive film having exposed and unexposed portions which is constituted essentially of a
60 polyhydroxybenzene, a fixed alkali accelerator, and a halide of a weak base.

4. A composition for treating light-sensitive film having exposed and unexposed portions which is constituted essentially of a
65 developer adapted to harden the exposed

portions, a fixed alkali accelerator, and an ammonium halide.

5. A composition for treating light-sensitive film having exposed and unexposed portions which is constituted essentially of a
70 polyhydroxybenzene developer, a fixed alkali accelerator, and ammonium chloride.

6. A composition for treating light-sensitive film having exposed and unexposed portions which is constituted essentially of a
75 hardener for hardening one of said portions, sodium hydroxide and a salt of a weak base.

7. A composition for treating light-sensitive film having exposed and unexposed portions which is constituted essentially of a
80 developer adapted to harden one of said portions, sodium hydroxide and a halide of a weak base.

8. A composition for treating light-sensitive film having exposed and unexposed portions which is constituted essentially of a
85 polyhydroxybenzene, sodium hydroxide and a halide of a weak base.

9. A composition for treating light-sensitive film having exposed and unexposed portions which is constituted essentially of a
90 developer adapted to harden the exposed portions, sodium hydroxide and an ammonium halide.

10. A composition for treating light-sensitive film having exposed and unexposed portions which is constituted essentially of a polyhydroxybenzene developer,
95 sodium hydroxide and ammonium chloride.

11. The art of treating light-sensitive film having exposed and relatively unexposed portions which comprises mixing
100 with a developer whose oxidization product is a hardener, a fixed alkali and a salt of a weak base in such proportions as to
105 convert the fixed alkali at least in part into an accelerator having less tendency to harden one of said portions of the film, and hardening the other of said portions of the film with the mixture.

12. The art of treating light-sensitive film having exposed and relatively unexposed portions which comprises mixing
115 with a polyhydroxybenzene, a fixed alkali and a halide of a weak base in such proportions as to convert the fixed alkali at least in part into an accelerator having less tendency to harden the unexposed portions of the film, and hardening the exposed
120 portions of the film with the mixture.

13. The art of treating light-sensitive film having exposed and relatively unexposed portions which comprises mixing
125 with a developer adapted to harden the exposed portion, sodium hydroxide and a halide of a weak base in such proportions as to convert the sodium hydroxide at least in part into an accelerator having less tendency to
130 harden one of said portions of the film, and

hardening the other of said portions of the film with the mixture.

14. The art of treating light-sensitive film having exposed and relatively unexposed portions which comprises mixing with a polyhydroxybenzene, sodium hydroxide and a salt of a weak base in such proportions as to convert the sodium hydroxide into an accelerator having less tendency to harden the unexposed portions of the film, and hardening the exposed portions of the film with the mixture.

15. The art of treating light-sensitive film having exposed and relatively unexposed portions which comprises mixing with a developer adapted to harden the exposed portion, a fixed alkali and an ammonium salt, thereby to form an ammonia accelerator, and hardening one of said portions with the mixture.

16. The art of treating light-sensitive film having exposed and relatively unexposed portions which comprises mixing with a polyhydroxybenzene, a fixed alkali and ammonium chloride, thereby to form an ammonia accelerator, and hardening said exposed portions with the mixture.

17. The art of treating light-sensitive film having exposed and relatively unex-

posed portions which comprises mixing with a hardener, sodium hydroxide and ammonium chloride, thereby to form sodium chloride and ammonium hydroxide, and hardening one of said portions with the mixture.

18. The art of treating light-sensitive film having exposed and relatively unexposed portions which comprises mixing with pyrogallic acid, sodium hydroxide and ammonium chloride, thereby to form sodium chloride and ammonium hydroxide, and hardening said exposed portions with the mixture.

19. A composition for treating light-sensitive film having exposed and unexposed portions which comprises a developer whose oxidation product is a hardener, sodium hydroxide, ammonium chloride, sodium chloride and ammonium hydroxide.

20. A composition for treating light-sensitive film having exposed and unexposed portions which comprises a polyhydroxybenzene, sodium hydroxide, ammonium chloride, sodium chloride and ammonium hydroxide.

Signed by me at Boston, Massachusetts
this nineteenth day of August 1922.

LEONARD T. TROLAND.