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TREATMENT OF PHOTOGRAPHIC FILMS AND PLATES

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18 Claims. (Cl. 95—7)

This invention relates to the treatment of photographic films, plates and other bodies having sensitized coatings thereon. For purposes of conciseness, the term "films" will be used herein, it being understood that this term is intended to cover not only films, but plates and other carrier bodies, for example paper, for the sensitized coating which, after exposure, is developed.

This application is a continuation-in-part of my copending application Serial No. 55,677, filed December 21, 1935.

When photographic developers are diluted, they often form a cloudy or turbid solution. This precipitation, even when it is almost colloidal in nature, has a very unfavorable effect on the developed image. I have found that this turbidity or cloudiness in the developing solution can be prevented by the addition to the developing solution of an alkali-metal metaphosphate or tripolyphosphate, for example sodium hexametaphosphate or sodium tripolyphosphate, either alone or in combination with alkali pyrophosphates. Instead of adding the alkali-metal metaphosphate or tripolyphosphate to the developing solution, I may add it to the gelatine colloid which is used in coating the photographic films.

All developing solutions are more or less alkaline in nature. Nearly all of them are prepared by the use of certain standard alkalis, such as sodium carbonate, borax, trisodium phosphate, and other similar alkalis which very readily form insoluble precipitates with the calcium and magnesium present in hard water. These precipitates may deposit out on the film which is being developed, thereby preventing the even development of the film and resulting in images which are not clear. The developing agents themselves consist, in general, of certain organic amines and phenols which, under certain conditions, may also react with the calcium and magnesium of hard water, thereby leading to rapid deterioration of the developing solution and slow and incomplete development of the film. The use of an alkali-metal metaphosphate or tripolyphosphate prevents the precipitation of calcium and magnesium salts and increases the effectiveness of the developing solution and produces more uniform results.

It is generally considered that the function of a photographic developer is to reduce to metallic silver or other metal those portions of the metallic salt used as a sensitizer which have been exposed to light, and the amount of reduction thus occurring is presumably directly proportional to the intensity of exposure at each individual point. Development of a film in this manner leads to a rather grainy image which is capable of only a moderate degree of enlargement without showing the granular clumps of image grain. Recent trends in photographic research have indicated that if this so-called purely chemical method of development can be combined with a so-called physical method of development in which the silver or other salt of the film is not only reduced by the developer, but is actually first redissolved and then reprecipitated out during the developing process, the resulting image is far more fine grained than the image obtained by purely chemical development. It is believed probable that when an alkali-metal metaphosphate or tripolyphosphate is present in the developing solution, it reacts with the silver or other salts in the emulsion, forming soluble silver or other metal complexes which, during development, are very slowly deposited out on the so-called activated nuclei in the emulsion. Thus, in a developing solution, the metaphosphate or tripolyphosphate probably performs two functions; first, it prevents the precipitation of insoluble calcium and magnesium salts of the developing agent itself and of the alkalies used with the developing agent and, secondly, it probably assists in transforming a purely chemical developer into a so-called physical developer with an accompanying improvement in the quality of the resulting image.

Beneficial effects are obtainable by adding the metaphosphate or tripolyphosphate to the emulsion used in forming the coating of the film. It also seems probable that when the metaphosphate or tripolyphosphate is used in the emulsion, the improved results may be due to reducing the concentration of certain ions such as iron, copper and aluminum by sequestering them in complex metaphosphate or tripolyphosphate compounds in which they do not have their usual deleterious effect of decreasing the transparency of the emulsion. The presence of these ions in their usual form in photographic emulsion may lead to spottiness in the photograph or may decrease considerably the sensitivity of the emulsion.

The amount of metaphosphate or tripolyphosphate used is dependent upon the purpose which it is desired to accomplish. To prevent turbidity in the developing solution a sufficient amount of the metaphosphate or tripolyphosphate to react with the calcium and magnesium in the water is added to the developing solution. Where the

metaphosphate or tripolyphosphate is used as a so-called physical developer, it should be present in higher amounts, probably two to four times the amount necessary to completely soften the water. The alkali-metal metaphosphates or tripolyphosphates may be used alone or in combination with an alkali-metal pyrophosphate, such as sodium pyrophosphate. The metaphosphates or tripolyphosphates are effective even when used in a developing solution having a pH value of 8 or higher.

The preferred alkali-metal metaphosphate is sodium hexametaphosphate sometimes called "Graham's salt." The preferred alkali-metal tripolyphosphate is sodium tripolyphosphate ($Na_5P_3O_{10}$). Chemical and X-ray analyses show that sodium tripolyphosphate is a definite chemical compound which is distinct from both sodium hexametaphosphate and sodium pyrophosphate and that it is not a mixture of the two. Sodium tripolyphosphate is fusible and may be solidified by very rapidly cooling in a glassy amorphous form. Under slower cooling it solidifies in the form of crystals. The glass may be converted into crystal form by annealing. Sodium tripolyphosphate forms a crystalline hydrate of the general formula $Na_5P_3O_{10}.6H_2O$. Sodium tripolyphosphate is colorless, appearing white in the granulated crystalline form. When crushed it forms a free-flowing granular mass. By suitable precautions it may be produced in a mass which readily disintegrates into its constituent fine crystals. Sodium tripolyphosphate is not deliquescent and particularly in its hydrated form may be preserved indefinitely in ordinary atmospheres without caking or picking up moisture. Sodium tripolyphosphate is readily water-soluble in both its glassy and crystalline forms.

The alkali-metal metaphosphates and tripolyphosphates are "molecularly dehydrated phosphates" as such term is employed in Hall and Jackson Patent No. 1,903,041. For example, sodium metaphosphate ($NaPO_3$) may be considered as derived from mono-sodium di-hydrogen orthophosphate by the removal of water of constitution. Likewise, sodium tripolyphosphate may be similarly considered as derived by molecular dehydration of a mixture of orthophosphates which is intermediate in acidity between the mono-sodium di-hydrogen orthophosphate and the di-sodium mono-hydrogen orthophosphate. The metaphosphates and tripolyphosphates may be regarded as salts of condensed or molecularly dehydrated phosphoric acids which have been molecularly dehydrated to a greater extent than pyrophosphoric acid.

Although slightly more of the sodium tripolyphosphate than the sodium hexametaphosphate is required to be added to the developing solution or to the sensitized emulsion, the sodium tripolyphosphate has the advantage that it is more stable in the alkaline developing solutions and therefore has less tendency than the hexametaphosphate to revert to the orthophosphate. The crystalline tripolyphosphate may be made without resorting to the drastic chilling required in producing the hexametaphosphate.

The invention is not limited to the development of films containing silver salts as the sensitizing agent, but is applicable in cases where other sensitizers are employed such as iron salts in blue and brown print paper, platinum salts in platino-type papers, and salts of gold used in gold-toning baths.

While I prefer to use sodium metaphosphate or sodium tripolyphosphate, the metaphosphates or tripolyphosphates of the other alkali-metals, such as potassium, lithium and ammonium, may be employed.

Although I have described certain preferred embodiments and methods of practicing the invention, it is to be understood that the invention is not limited thereto, but may be otherwise embodied or practiced within the scope of the following claims.

I claim:

1. A photographic film having a sensitized coating containing an alkali-metal salt of a phosphoric acid which is molecularly dehydrated to a greater extent than pyrophosphoric acid.

2. A photographic film having a sensitized coating containing an alkali-metal metaphosphate.

3. A photographic film having a sensitized coating containing an alkali-metal tripolyphosphate.

4. The method of preventing precipitation of insoluble salts of alkaline earth metals in photographic gelatino-silver halide emulsions which comprises adding to the emulsion an alkali metal salt of hexametaphosphoric acid.

5. The method of preventing precipitation of insoluble salts of alkaline earth metals in photographic gelatino-silver halide emulsions which comprises adding sodium hexametaphosphate to the emulsion.

6. A gelatino-silver halide photographic emulsion containing an alkali metal salt of hexametaphosphoric acid.

7. A gelatino-silver halide photographic emulsion containing sodium hexametaphosphate.

8. The method of preventing precipitation of insoluble salts of alkaline earth metals in photographic gelatino-silver halide emulsions, which comprises adding to the emulsion an alkali-metal salt of metaphosphoric acid.

9. The method of preventing precipitation of insoluble salts of alkaline earth metals in photographic gelatino-silver halide emulsions, which comprises adding sodium metaphosphate to the emulsion.

10. A gelatino-silver halide photographic emulsion containing an alkali-metal salt of metaphosphoric acid.

11. A gelatino-silver halide photographic emulsion containing sodium metaphosphate.

12. A photographic film having a gelatino-silver halide coating containing an alkali-metal salt of a phosphoric acid which is molecularly dehydrated to a greater extent than pyrophosphoric acid.

13. A photographic film having a gelatino-silver halide coating containing an alkali-metal metaphosphate.

14. A photographic film having a gelatino-silver halide coating containing an alkali-metal tripolyphosphate.

15. The method of preventing precipitation of insoluble salts of alkaline earth metals in photographic gelatino-silver halide emulsions, which comprises adding to the emulsion an alkali-metal salt of a phosphoric acid which is molecularly dehydrated to a greater extent than pyrophosphoric acid.

16. The method of preventing precipitation of insoluble salts of alkaline earth metals in photographic gelatino-silver halide emulsions, which comprises adding to the emulsion a sodium salt of a phosphoric acid which is molecularly de-

hydrated to a greater extent than pyrophosphoric acid.

17. A gelatino-silver halide photographic emulsion containing an alkali-metal salt of a phosphoric acid which is molecularly dehydrated to a greater extent than pyrophosphoric acid.

18. A gelatino-silver halide photographic emulsion containing a sodium salt of a phosphoric acid which is molecularly dehydrated to a greater extent than pyrophosphoric acid.

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