

UNITED STATES PATENT OFFICE

2,256,390

METHOD OF PREVENTING PRECIPITATION
OF ALKALINE-EARTH METAL SALTS IN
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mesne assignments, to Eastman Kodak Com-
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JerseyNo Drawing. Application August 19, 1936,
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2 Claims. (Cl. 95-7)

This invention relates to photographic gelatin and emulsions and particularly to a method for preventing precipitation of insoluble salts in gelatin solutions and emulsions.

Difficulties have often been encountered when certain solutions, emulsions, or suspensions are added to gelatin solutions or photographic emulsions used for coating light sensitive plates, films, and papers, by reason of the separation of insoluble calcium, magnesium, or other alkaline-earth metal salts which are formed by the interaction of soluble salts of these metals contained in the gelatin solution or photographic emulsion with some constituent of the solution, emulsion, or suspension added. This effect is undesirable for a number of reasons. The coatings, produced by the gelatin or photographic emulsion in which a soluble salt has been precipitated, are cloudy or hazy and not fully transparent as desired for photographic uses, and another objection is that the active ingredients of the solution added to the gelatin or photographic emulsion may be wholly or partially precipitated and thereby prevented from having the desired effect on the gelatin solution or photographic emulsion.

It is, therefore, an object of the present invention to provide a method for preventing precipitation of insoluble salts of alkaline-earth metals in gelatin solutions and emulsions. A further object is to provide a method for the clarification of gelatin solutions and emulsions. A still further object is an improved photographic emulsion free from haze. Other objects will appear from the following description of my invention.

These objects are accomplished by adding an alkali-metal salt of hexametaphosphoric acid to the gelatin solution or photographic emulsion or to the solution or emulsion to be added to the gelatin solution or photographic emulsion.

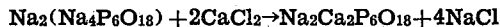
The alkali-metal salts of hexametaphosphoric acid have the property of forming soluble complex ions with ions of calcium, magnesium and other alkaline earth metals and this results in lowering the concentration of these metallic ions to such a value that they are no longer precipitated by acidic ions or radicals such as carbonate, sulphate, oxalate, oleate, and other fatty acid radicals etc. Other heavy metal ions such as iron and aluminum also form complex ions with hexametaphosphates which are soluble in solution but these complex ions are formed to a lesser degree.

Although I do not wish to commit myself to the following explanation of the reason for this effect, I believe that the mechanism of the re-

action involved may be explained in the following way: When sodium metaphosphate is heated to a temperature of about 620° C., it passes into the hexametaphosphate according to the following reaction:



When the sodium hexametaphosphate is added to a solution containing a calcium or other alkaline-earth metal compound, a double salt of sodium and calcium or other alkaline-earth metal is formed according to the following reaction:



This double salt of sodium and calcium ionizes in solution to sodium ions and calcium hexametaphosphate ions both of which are soluble. The calcium ions are bound up in the hexametaphosphate radical and are not produced as free calcium ions in the solution. This ionization may be represented as follows:



In addition to sodium hexametaphosphate, other alkali-metal salts of hexametaphosphoric acid may be employed such as the lithium and potassium salts.

This property of the alkali-metal salts of hexametaphosphoric acid may be taken advantage of in a number of ways in connection with photographic gelatin and emulsions. One use is the clarification of gelatin solutions. Many solutions of gelatin are cloudy or hazy due to the presence of finely suspended matter, which in many cases consists largely of insoluble calcium salts. The addition of sodium hexametaphosphate to a gelatin solution containing a haze of such material lowers the concentration of calcium ions in the solution to such an extent that a greater amount of calcium salt dissolves. This process is repeated until finally all of the calcium salt passes into solution and the gelatin becomes clear. The amount of sodium hexametaphosphate necessary to achieve this result will vary with the condition of the gelatin and the amount of calcium salt present. In general, about 8.0% of sodium hexametaphosphate as reckoned on the amount of gelatin, will be sufficient. This amount may vary, however, from ½% to about 20.0%, depending on the quantity of calcium, or other alkaline earth metals, present.

Another important use of this property of the alkali-metal hexametaphosphate is in connection with the addition of wax emulsions to photo-

graphic emulsions for the manufacture of self-lubricating films. The addition of wax emulsions to photographic emulsions for this purpose is described in the patent of E. J. Ward, No. 2,059,829, granted November 3, 1936. Wax emulsions are readily flocculated and coagulated by small amounts of ions of calcium, magnesium, and other alkaline-earth metals and in fact, most heavy metals. Photographic emulsions and gelatin solutions, however, rarely contain more than slight traces of metallic ions other than those of magnesium and the other alkaline-earth group; and it is in connection with this group that the hexametaphosphates are most effective.

I have found that the flocculation of wax emulsions upon addition to photographic emulsions or gelatin solutions may be prevented by adding sodium hexametaphosphate to the wax emulsion or to the photographic emulsion or gelatin solution before the mixture is made. The sodium hexametaphosphate must be added in sufficient amount to react with all of the metal ions which tend to flocculate the wax emulsion. The following formulas have been found satisfactory.

Example I

Three solutions or emulsions are made up as follows:

	Grams
A. Sodium hexametaphosphate	9
Water	81
B. Photographic emulsion	5000
C. Wax emulsion (20% wax)	100
Water	210

In making up the finished photographic emulsion containing wax, the solution A, which is made by dissolving the hexametaphosphate in water, is added to the photographic emulsion B. The wax emulsion is added to water to form the emulsion C, which is then added slowly to the mixture of A and B with stirring. Any suitable natural or synthetic wax such as that disclosed in the Ward Patent No. 2,059,829 may be used. A preferred wax is carnauba wax.

Example II

Solutions or emulsions are made up as follows:

	Grams
A. Sodium hexametaphosphate	9
Water	291
B. Wax emulsion (20% wax)	100
C. Photographic emulsion	5000

The hexametaphosphate is dissolved in water to

make solution A. To this is added the wax emulsion B slowly with stirring. The mixture of A and B is then added slowly with stirring to the photographic emulsion C.

In the above examples, I have referred to mixing the wax emulsion with sensitive photographic emulsions. It should be understood, however, that the wax emulsion may be mixed with gelatin solutions for use as backings, undercoats, or overcoating layers for photographic films.

Another use of alkali-metal hexametaphosphates according to my invention, is in the manufacture of the suspension of finely divided manganese dioxide by the reduction of potassium permanganate. When manganese dioxide is manufactured in this way, carbon dioxide is frequently liberated and if the suspension is mixed with gelatin, the carbon dioxide thus produced precipitates insoluble carbonates from the gelatin solution since the gelatin frequently contains alkaline-earth metal compounds. The precipitation of these insoluble salts may be prevented by the addition of the hexametaphosphate to the gelatin solution before the reduction of the potassium permanganate takes place.

A further use for the compounds according to my invention is in the incorporation of certain dyes in gelatin solutions or emulsions. Dyes such as sulfonated aryl amino ethyl alcohols of the Ionamine type are precipitated by calcium and similar ions. This property has heretofore limited the use of these dyes in photographic gelatin. With the aid of sodium hexametaphosphate, such precipitation can be readily prevented either by adding the hexametaphosphate to the dye solution or to the emulsion or solution of gelatin to which the dye solution is to be added.

It is to be understood that my invention may be used in other ways and that the compounds may be employed in other proportions than those specifically mentioned in the preceding description of my invention. I intend my invention to be limited only by the scope of the appended claims.

I claim:

1. The method of incorporating wax in a gelatin photographic emulsion, which comprises adding an alkali metal salt of hexametaphosphoric acid to the gelatin emulsion, and mixing the wax emulsion with the gelatin emulsion.

2. The method of incorporating wax in a gelatin photographic emulsion, which comprises adding sodium hexametaphosphate to the gelatin emulsion, and mixing the wax emulsion with the gelatin emulsion.

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