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PROCESS OF PRESERVING PHOTOGRAPHIC GELATINOUS COMPOSITIONS FROM DECOMPOSITION

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This invention relates to a process for preserving proteinaceous substances from decomposition and especially to the good preservation of photographic gelatin, either as a solution when preparing the emulsion and when storing before coating or as a layer in a photographic material.

It is generally known to use formol, phenol, thymol, esters of p-hydroxybenzoic acid, e.g., methyl-, ethyl-, propyl- and butylesters, as preservatives for gelatin.

It is further known that chlorinated phenols, e.g. pentachlorophenol, quaternary ammonium salts or mercury compounds may be used as preservatives or as disinfectants.

Some of the above mentioned products must be used in large amounts to be effective. Others are poorly soluble in water and moreover difficultly miscible with aqueous protein solutions. Still others impair the sensitivity or produce fog in the photographic emulsions.

It has now been found that gelatinous photographic compositions may be preserved most efficiently from decomposition by the use of 0.1 to 1% based on the weight of dry gelatin of a single or a mixed salt of cerium, erbium, lanthanum, neodymium, praseodymium, samarium, scandium and/or yttrium.

In general these salts are marketed as mixed salts of several of these metals or sometimes as mixed salts of these metals with other metal salts. These mixtures are markedly cheaper than any of the single salts.

The addition of compounds of said metals to solutions or layers of gelatin or proteins for preserving them from decomposition, scarcely or not influences the physical properties of the solutions or layers and particularly does not show the drawbacks of the hitherto known products.

The required amount of products to hinder the growth of micro-organisms and moulds is not critical but very good results are obtained by adding 0.1 to 1% of salts of said metals based on the weight of dry gelatin.

For the other purposes for which these products were already known, namely as hardening and coagulating agents for gelatin, the amounts to be used are much larger and it was thus completely surprising that from the use of quantities so small as 0.1 to 1% such effective preservation of the photographic gelatino silver halide emulsion arises. Thus the use of such compounds is also allowable in circumstances wherein such coagulation or hardening is not desired.

The products may be added to the coating solution before as well as after coating by immersing the material in a solution of salts of scandium and/or of yttrium and/or of rare earth metals.

The following examples illustrate the invention without limiting, however, the scope thereof.

Example 1

To 100 cm.³ of a 10% aqueous gelatin solution are added 2 cm.³ of a 1% aqueous solution of samarium nitrate. The pH is adjusted to 7. This solution as well as a comparison solution without samarium nitrate are infected with putrefactive bacteria. The solutions are brought into test-tubes. After storage at room temperature for a week, the comparison solution deliquesces, while even after 3 months no deliquescence occurs in the solution containing samarium nitrate.

Example 2

Similar results as in Example 1 are obtained by substituting the 2 cm.³ of 1% aqueous solution of samarium nitrate for 4 cm³ of a 1% aqueous solution of neodymium chloride.

Example 3

To 1 kg. of an extremely sensitive photographic silver halide emulsion containing 80 g. of dry gelatin are added 32 cm.³ of a 1% aqueous solution of yttrium nitrate. The solution and the corresponding layers coated from this solution are protected against micro-organisms. The sensitivity, the fog and the contrast of the emulsion are not impaired.

Example 4

To 100 cm.³ of a 10% aqueous solution of gelatin is added 1 cm.³ of a 1% aqueous solution of yttrium nitrate. The pH is adjusted to 6.5. 15 cm.³ of this solution are brought into a Petri-dish and solidified. The obtained solid as well as a comparison solution without yttrium nitrate are locally infected with putrefactive bacteria. After storage at room temperature for a week, the comparison solution deliquesces while even after 1 month no deliquescence occurs in the gelatin solution containing yttrium nitrate.

Example 5

An X-ray film is developed, fixed, rinsed, brought for 5 minutes into a 0.1% aqueous solution of yttrium nitrate, and dried. Chemical analysis shows that the film now contains 0.3% of yttrium nitrate based on the weight of dry gelatin. By prolonging the time of immersion the concentration of yttrium nitrate rises to 0.5%. The film as well as the comparison material which has not been treated with the yttrium nitrate solution are grafted with mould. After a week the comparison material which has not been treated with yttrium nitrate shows growth of mould, while even after 1 month no growth of mould is observed on the film rinsed with a solution of yttrium nitrate.

Example 6

To 100 cm.³ of a 5% aqueous solution of gelatin are added 5 cm.³ of a 1% aqueous solution of cerium nitrate. The pH is adjusted to 7. 15 cm.³ of this solution are brought in a Petri-dish, solidified and locally infected with liquefying bacteria. The same test is carried out with a gelatin gel without cerium nitrate. After a few days the gelatin gel without cerium nitrate deliquesces while after 4 weeks, deliquescence has not yet occurred with the gelatin containing cerium nitrate.

Example 7

To 500 cm.³ of an 8% aqueous solution of gelatin are added 16 cm.³ of a 1% aqueous solution of lanthanum nitrate. The pH is adjusted to 7. This gelatin solution is protected against bacteria growth. In layers coated from this solution the presence of the lanthanum nitrate seems also to hinder the growth of mould.

We claim:

1. A photographic gelatino silver halide emulsion layer containing 0.1 percent to 1.0 percent, based on the weight of the dry gelatin, of at least one chloride selected form the group consisting of cerium, lanthanum, neodymium, samarium, and yttrium.

2. A photographic gelatino silver halide emulsion layer containing 0.1 percent to 1.0 percent, based on the weight of the dry gelatin, of at least one nitrate selected

from the group consisting of cerium, lanthanum, neodymium, samarium, and yttrium.

3. Photographic gelatino silver halide emulsion containing 0.4% of yttrium nitrate based on the weight of dry gelatin.

4. X-ray film containing gelatino silver halide emulsion layers and 0.3% to 0.5% of yttrium nitrate, based on the weight of dry gelatin.

5. Photographic gelatino silver halide emulsion layer containing 0.4% of yttrium nitrate based on the weight of dry gelatin.

6. Photographic gelatino silver halide emulsion layer containing 0.3% to 0.5% of yttrium nitrate based on the weight of dry gelatin.

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