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PHOTOGRAPHIC EMULSION

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This invention relates to photographic emulsions and particularly to the preparation of fine grain emulsions.

The preparation of peptization emulsions using gelatin as the protective colloid is well known. Peptization emulsions are those in which the silver halide grains are formed by precipitation in an aqueous solution and are subsequently dispersed in a colloidal medium. It is desirable with peptization emulsions as with other emulsions that the size of the silver halide grains should be small so that the resulting image may be enlarged or magnified without exhibiting undue graininess. In general, however, if the silver halide grains are small, the sensitivity of the emulsion is less than it would be if the grain size were greater. It is desirable, therefore, to produce a fine grain emulsion in which the speed or sensitivity is comparable with that of emulsions of larger grain size.

I have found that peptization emulsions of satisfactory sensitivity and fine grain size may be produced by substituting citrous pectin for the gelatin ordinarily used in the production of peptization emulsions. I have also found that it is possible to use pectin as a substitute for gelatin in the preparation of photographic emulsions in which the precipitation of silver halides is carried out in the presence of the protective colloid rather than in the presence of water as in the case of peptization emulsions. Emulsions so prepared have finer grain than those in which the precipitation is carried out in gelatin.

In the poduction of peptization emulsions according to my invention, pectin is dispersed in an aqueous solution of potassium bromide. It has been found that pectin dispersed better in solutions of potassium bromide than in pure water and that it is desirable to use excess bromide with or without ammonia or other silver solvents in conjunction with the pectin during the peptizing operation. Silver halide is precipitated in a separate aqueous solution, for example, by mixing an alkali metal halide with silver nitrate. The pectin solution is then added to the precipitated silver halide, and the resulting emulsion is digested for a specified time and temperature, then cooled and gelled.

It is necessary to add photographic gelatin to the emulsion after the pectin has been added to the silver halide and before the heating operation. This enables the resulting emulsion to be solidified for subsequent operations such as washing and finishing to the optimum photographic conditions. The dispersed pectin is miscible with photographic gelatin. In order to obtain an emulsion which sets satisfactorily, the ratio of pectin to gelatin should not be greater than 1 to 2.

I have also found that pectin may be used as a substitute for gelatin in the preparation of photographic emulsions in which the precipitation of the silver halide is carried out in the presence of a protective colloid. According to this method, pectin is substituted for gelatin in the usual emulsion making procedure. Emulsions so prepared are finer grained than those made with gelatin but it is necessary to control the pH of the emulsion since, if the pH is above seven, the emulsion is susceptible to fog. When used in this way, pectin was found to be effective as a dispersing medium at concentrations as low as 0.03%.

The pectin used in the production of photographic emulsions according to my invention was obtained as a commercial product from the California Fruit Growers Exchange and contained a small amount of refined corn sugar to control its gelling power. It was produced by the extraction of the pulp of citrous fruit skins after the removal of the fruit oils present in such skins, the pectin having been isolated by precipitation of such extracts in alcohol.

Pectin as a substitute for gelatin was found particularly useful in making emulsions having a high ratio of silver halide to colloid. For example, it was found possible to prepare an emulsion with a ratio of silver halide to colloid as great as 6 to 1. Pectin was also found to act more effectively as a dispersing colloid at high temperatures.

The following example illustrates the formation of a peptization emulsion according to my invention. Three solutions were prepared as follows:

A. 60 grams of potassium bromide were dissolved in 150 cc. of water and the solution heated to 85° C. To this solution there were added, with vigorous stirring, 5 grams of citrous pectin, and the solution was held at 85° C.

B. 190 grams of potassium bromide and 0.75 gram of potassium chloride were dissolved in 2640 cc. of water and the solution cooled to 10° C. or less.

C. 300 grams of silver nitrate were dissolved in 300 cc. of water and cooled to 10° C. or less.

The silver nitrate solution C was poured into the potassium halide solution B and kept cold while stirring. The mixture was stirred for about two minutes and the grains were then allowed to settle for 15 minutes. When the grains had settled, about 2100 cc. of the supernatant liquid was poured off and the hot pectin solution was added to the residue of silver halide grains with thorough stirring. The temperature of the resulting emulsion was raised to 85° C. in about 15 minutes. When a temperature of 85° C. had been reached, 45 grams of deashed gelatin was added and the emulsion cooked at 85° C. for 20 minutes. It was then cooled until the emulsion had gelled.

After 24 hours cold storage, the emulsion was shredded and washed to a bromide ion concentration of 5×154 moles per liter. It was heated to the desired finishing temperature and coated.

Peptization emulsions containing varying amounts of gelatin were compared with similar emulsions containing varying amounts of pectin. Each of these emulsions was exposed on an Eastman Type II-B Sensitometer and was developed for four minutes at 65° F. in a developer having the following composition:

Monomethyl-p-aminophenol sulfate	grams	2.2
Sodium sulfite (desiccated)	do	96
Hydroquinone	do	8.8
Sodium carbonate (desiccated)	do	48
Potassium bromide	do	5
Water to	liters	1

For each of these coatings the speed, gamma and fog were measured and recorded and the graininess was estimated on the basis of the relative scale of degrees indicated by the successive numbers 1, 2, 3, 4, 5, etc., with the finer grain indicated by the lower number. The results thus obtained are shown in the following table:

Name of substance	Percent in water volume	Unsensitized speed	Gamma	Fog	Grain
Gelatin	1.3	135	1.81	.05	5
Do	0.64	135	2.23	.08	5-6
Do	0.32	180	1.87	.04	5
Do	0.06	170	1.50	.04	5
Pectin (citrous)	1.3	64.5	2.43	.05	2-3
Do	0.64	79.5	1.98	.06	2-3
Do	0.32	63.0	2.05	.05	2-3
Do	0.06	135.0	1.53	.04	4

The results obtained as shown by the above table indicate that, although the speed of the emulsions prepared from pectin was slightly less than in the case of the corresponding emulsion prepared with gelatin, the gamma and fog results were comparable. The graininess was much less since, on the relative scale used, 5 indicates two degrees more grain than 2-3, and more grain than 4. A satisfactory reduction in grain without a large decrease in speed was found to have been effected.

It is to be understood that various modifications may be made in the details described herein without departing from the invention and that my invention is to be taken as limited only by the scope of the appended claims.

I claim:

1. In the method of preparing a photographic peptization emulsion, the steps which comprise precipitating silver halide in water, cooling the aqueous precipitate, and mixing it with a hot pectin solution while maintaining the pH below 7.

2. The method of preparing a photographic peptization emulsion which comprises precipitating silver halide in water, cooling the aqueous precipitate, mixing it with a hot pectin solution while maintaining the pH below 7, and adding gelatin to the resulting emulsion.

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