

UNITED STATES PATENT OFFICE

2,565,418

METHOD OF PREPARING PHOTOGRAPHIC
SILVER HALIDE EMULSIONSEdward C. Yackel, Rochester, N. Y., assignor to
Eastman Kodak Company, Rochester, N. Y., a
corporation of New JerseyNo Drawing. Application August 13, 1947,
Serial No. 768,511

5 Claims. (Cl. 95-7)

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This invention relates to the preparation of photographic emulsions having silver halide as the sensitive element in which the silver halide is prepared in dispersed form in gelatin and is then mixed with a high polymer compound containing carboxyl groups therein, followed by coagulation with acid and washing. The invention also includes the washed silver-halide dispersions and the emulsions obtained by re-dispersing the washed silver-halide grains in a vehicle therefor.

The most common method of preparing silver-halide dispersions is by reacting a water-soluble silver salt, such as silver nitrate and a water-soluble halide, such as potassium bromide in an aqueous solution of a peptizing agent, usually gelatin. There results from this operation a dispersion of the silver halide in an aqueous solution of the gelatin or other peptizing agent, which solution also contains salts resulting as a by-product of the reaction. In processes of making silver-halide dispersions and emulsions using the natural product, gelatin, the emulsion maker has in the past been limited in the scope of his operations by the physical properties of that material. For instance, concentrations of silver halide and of gelatin have had to be used which are not necessarily most desirable in photographic products. Also, in reducing the proportion of soluble salts in the emulsion to a minimum, many difficulties have been met with. It has been the practice previously where gelatin has been used as the dispersing material to remove the soluble materials therefrom by setting the gelatin dispersion, noodling and then washing the noodles by osmosis in cold water having a hardening agent therein. Under such conditions a minimum gelatin concentration of approximately 4% is necessary, and this limitation has hampered the operations of the emulsion maker in his preparation of emulsions of this type.

One of the objects of my invention is to prepare dispersions of silver halides from which water-soluble by-products may be readily removed. Another object of my invention is to provide a method of preparing silver-halide dispersions in which the dispersing material may be reduced to a small percentage. A further object of my invention is to provide a method of washing silver-halide dispersions in which substantially all of the liquid may be removed, thus making for substantially complete removal of the water-soluble impurities therein. Other objects of my invention will appear herein.

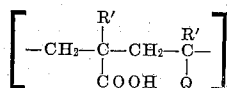
In its broadest aspects my invention comprises

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the preparation of silver halide in an aqueous solution of a dispersing agent or peptizer and then adding to the dispersion a small proportion of a high polymer compound containing carboxyl groups therein which is soluble under alkaline conditions but insoluble when the pH of the dispersion is reduced. The dispersion so formed is then acidified precipitating the dispersed material in the form of silver-halide grains enveloped in the colloidal material which is present. These grains are readily susceptible to washing either once or several times and may then be redispersed by raising the pH value and subsequently may be mixed with a protective colloid to form a uniform photographic emulsion. My invention offers a simple means of preparing emulsions of high silver concentration which is especially valuable in the manufacture of photographic films bearing large quantities of silver per unit area.

Any of the high polymer compounds containing carboxyl groups therein may be employed in proceeding in accordance with my invention. Some of the high polymer materials which may be used are:

1. Those resins having the formula:

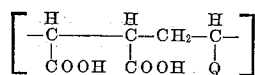


Q=halogen, COR, COOR, H, CN or $\text{O}=\text{C}-\text{R}$

R=H, alkyl or aryl

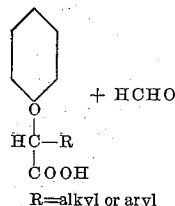
R'=H, methyl, NO₂ or NH₂

2. Those resins having the formula:



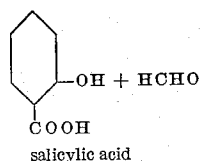
Q=halogen, COR, COOR, H, CN, alkyl, aryl or $\text{O}=\text{C}-\text{R}$

3. Those resins resulting from the reaction between a phenoxy acetic acid and formaldehyde, such as



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4. Those resins resulting from the reaction between hydroxy aromatic acids and formaldehyde as illustrated by the following:



5. The hemi-esters of polymeric hydroxyl-containing compounds.

6. The polyanhydro uronic acids.

The resins of class 1 are illustrated by the products obtained by polymerizing methacrylic acid with various monomers such as butyl methacrylate, methyl methacrylate, styrene or methylacrylate depending on the product desired. Class 2 is illustrated by the styrene-maleic anhydride resins. An example of the compounds of the type of class 3 are the resins formed by the copolymerization of phenoxy acetic acid and formaldehyde. Class 4 is illustrated by the polymer formed by the copolymerization of salicylic acid and formaldehyde. Class 5 is illustrated by polyvinyl phthalate or polyvinyl succinate, the making of which is described in Malm et al. Patent No. 2,379,309 or cellulose acetate phthalate, the making of which is described in Malm and Waring Patent No. 2,093,462. The high polymer materials of class 6 are illustrated by alginic acid which is a commercial product obtained from seaweed or the oxidized cellulose obtained by treating cellulose with NO_2 , such as described in Kenyon and Yackel Patent No. 2,232,990. These high polymer compounds have been found by me to be most useful for preparing washed dispersions of silver halide in accordance with my invention. The alkyl resins have also been found to be useful in preparing photographic emulsions as described herein.

My invention is carried out by first mixing a water-soluble silver salt and a water-soluble halide in an aqueous solution of a peptizer, particularly gelatin under high-speed agitating conditions. If desired, the aqueous silver salt and the aqueous halide may be run into the aqueous solution of peptizer while rapidly agitated. Instead of this, the peptizing agent may be mixed with the halide and only the silver salt solution be run into the mass. After the silver-halide dispersion has been prepared, it is then mixed with an aqueous solution of a high polymer compound containing carboxyl groups, the latter being used as an aqueous solution in the form of its alkali metal salt. It is necessary to keep the pH of the solution above 6.5 to avoid any local precipitation action while mixing the silver salt dispersion. After thoroughly incorporating the high polymer compound in the silver-halide dispersion, the pH of the mass is lowered by the addition of an aqueous acid, such as dilute aqueous sulfuric acid, to a pH of 4 to 5.5. After the addition of the acid with thorough mixing, coagulation of the silver-halide system including the resin and the peptizer used will occur. The insoluble material settles in the form of silver-halide grains enveloped with the peptizing agent and the high polymer material which was added. After the coagulum has settled and the liquid thereon has been decanted off, the grains of silver halide are washed by using a quantity of distilled water at 20° C. The mass is stirred, such as for a minute or two and the silver-halide grains are then allowed to settle and decanted as before.

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The resulting washed coagulum may then be mixed with a gelatin solution, the pH raised to at least 6.5 by the addition of a dilute aqueous alkaline material, such as ammonium hydroxide, and the mass stirred at a temperature of 30° C. or higher to redisperse the coagulum. The material so prepared is then employed for photographic purposes with or without additional sensitization as well known in the art. The high polymer material containing carboxyl groups therein is ordinarily added to the dispersion of the silver halide in the peptizer after the dispersion is prepared in the proportion of $\frac{1}{3}$ to 1 part of the high polymer material per part of gelatin, or other dispersing colloid, which has been employed. The compounds are ordinarily added in the form of 10% aqueous solutions of their alkali or ammonium salts, and the solutions are adjusted, before addition to the dispersion, to a pH of 6.5 or higher. Whether or not a proportion of the high polymer compound in the higher or lower portion of the range given is used depends to some extent upon the ratio of gelatin (or other peptizer) to water and also to some extent upon the type of high polymer compound which is employed. Higher ratios of the high polymer compound, even than 1 to 1, might be employed but ordinarily it is most desirable to operate in the range given.

The coagulation of the high polymer compounds is ordinarily carried out by the addition of acid, such as sulfuric acid to reduce the pH to the range of 4 to 5.5. In many cases a pH of approximately 4.7 is advantageous. The acid which may be employed here is any inert acid which will not have any deleterious effect upon the photographic material being prepared. Instead of sulfuric acid, acetic acid or phosphoric acid are quite suitable for use in this connection. The washing operation may then be carried out by applying purified water, particularly distilled water to the coagulated grains, allowing to stand so that the grains settle and decanting or otherwise separating the liquid from the grains. This may be repeated, if desired, but ordinarily the number of washings is limited to one to four. If desired, after one washing or in lieu of any washing, the coagulum may be re-dispersed and again coagulated thus serving to remove further water-soluble materials.

The coagulation is preferably carried out at a temperature within the range of 30° to 50° C. although in certain cases higher or lower temperatures may be useful. The choice of the temperature employed is ordinarily governed by the conditions of concentration, and the nature of the high polymer compound used in connection with the physical characteristics of the coagulum which is desired. For instance, other conditions being equal, a lower temperature usually tends to give a coagulum of a more flocculent or granular form which requires greater time to separate from the mother liquor. Higher temperatures, on the other hand, favor the formation of a pasty form of this solid phase which may tend to agglomerate into clumps or adhere to the sides of the beaker. Therefore, it is usually desirable to operate within the 30-50° C. range to obtain the best results.

In the preparation of emulsions in accordance with my invention it is to be understood that the various treatments peculiar to emulsion making may be applied to emulsions prepared in accordance with my invention. For instance, emulsions prepared in accordance with my invention may be ripened by subjecting to an elevated

temperature for a time or may be sulfur-sensitized by adding allyl thiourea or some other sulfur-containing compound thereto or may be optically sensitized by the addition of a sensitizing dye. The sensitometric result of emulsions prepared in accordance with my invention show that the finished products do not appreciably differ from similar ones which have been prepared heretofore. It is also to be understood that included within the scope of my invention is the use of mixtures of high polymer compounds containing carboxyl groups therein. For instance, some compounds of that nature are better as regards coagulating power than others. Then again, other compounds of this nature may exhibit re-dispersing powers superior to other compounds of this nature. It is useful in cases of that type to mix two or more high polymer compounds, such as specified herein to obtain the desired characteristics.

The following examples illustrate my invention:

Example 1.—100 parts of silver nitrate were dissolved in 900 parts of distilled water at 25° C. A separate solution was prepared by dissolving 80 parts of potassium bromide and one part of potassium iodide together with 27 parts of photographic gelatin in 900 parts of distilled water. The temperature of this second mixture was elevated to 50° C. and stirring was employed to dissolve the gelatin. The silver nitrate solution was then added slowly over a period of about ten minutes at 50° C. with stirring. The mass was then stirred at 50° C. for ten minutes, cooled to 40° C., and 150 parts of a 10% aqueous solution of a salicylic acid-formaldehyde resin were added thereto in the form of its sodium salt. The pH of this solution was approximately 6.5. The solution was thoroughly mixed for one minute, and the pH was then adjusted to 4.75 with dilute aqueous sulfuric acid. Coagulation of the gelatin-resin-silver-halide system occurred. The coagulum was allowed to settle, and the mother liquor was decanted therefrom. The mother liquor was replaced with an equivalent quantity of distilled water at 20° C. The mass was stirred for two minutes and was allowed to settle. The liquid present was decanted as before. There was then added to the coagulum 150 parts of photographic gelatin dissolved in 1500 parts of distilled water at 40° C. The mass was stirred and the pH was adjusted to 6.5 by the addition of dilute ammonium hydroxide. Stirring was continued until complete re-dispersion of the silver-halide grains was obtained. The mass was then warmed for a time to obtain optimum photographic speed and was found to be useful for preparing photographic products being capable of being coated onto either glass, paper, or film support as desired.

Example 2.—The procedure of the preceding example was repeated except that a mixture of 75 parts of a 10% solution of phenoxy acetic acid-formaldehyde resin and 75 cc. of a 10% solution of polyvinyl phthalate resin, both in the form of their sodium salts, was employed instead of the salicylic acid-formaldehyde resin in the preceding example. Here again an emulsion was obtained which was useful for forming photographic products by coating upon suitable support.

Example 3.—To a fine-grain positive emulsion containing 25 gms. of gelatin for a total of 3500 cc., was added 15 gms. of a glycerol-phthalic anhydride resin (ordinarily known as alkyd res-

in), having an acid number of 154, as the sodium salt. The resin was added as a 10% aqueous solution adjusted to a pH of 6.5 with NaOH. The mass was thoroughly mixed and the pH was adjusted to 4.75 with dilute aqueous sulfuric acid. Coagulation of the silver halide grains enveloped by the colloid present occurred. The coagulum was allowed to settle and was separated from the supernatant liquor. An equivalent quantity of distilled water was added to the coagulum, the mass was thoroughly stirred and was allowed to settle. The coagulum was again separated from the liquid. The coagulum was then mixed with 150 parts of gelatin dissolved in 1500 parts of distilled water at 40° C. The pH was adjusted to 6.5 with ammonium hydroxide and the mass was stirred until complete redispersion of the silver halide grains was obtained. The mass was then warmed for a time to obtain optimum photographic speed and was found to be useful for preparing photographic products being capable of being coated onto either glass, paper or film support, to form photographic products.

The polymeric materials which are useful in my invention result from the polymerizing of at least 6 units of the monomers employed in their preparation and, as a general rule, comprise at least 12 and up to 100 or even more. The criterion of the usefulness of the polymeric materials is that they contain sufficient carboxyl to render those materials soluble in the presence of alkali but insoluble under acidic conditions. In the case of those copolymers in which methacrylic acid is copolymerized with other monomers, such as butyl methacrylate, methyl methacrylate, styrene, or the like, a minimum carboxyl content of at least 14 or 15% is desirable. With resins of the styrene-maleic anhydride type, a minimum carboxyl content of 25% is required. With resins of the phenoxy acetic acid-formaldehyde type 15% of carboxyl is the minimum desired as is also true of the salicylic acid-formaldehyde type resins. With polyvinyl phthalates or succinates the minimum carboxyl content should be at least 25%. In the case of cellulose which has been oxidized with NO₂ a minimum carboxyl content determined by the uronic acid method of at least 12% is desirable. With alkyd resins a minimum carboxyl content of at least 12% is desired. It is to be understood that all of these carboxyl contents are by weight.

It is to be understood that the preparation of silver-halide dispersions and emulsions are carried out under darkened conditions so that the photographic products prepared therefrom retain their sensitiveness until exposed in actual use.

I claim:

1. A method of preparing acid coagulable silver-halide dispersions of low water soluble salt content which comprises preparing silver-halide in an aqueous solution of a silver-halide dispersing agent, mixing therewith $\frac{1}{2}$ -1 part of an alkali-soluble, acid-insoluble organic resin containing carboxyl groups, per part of silver-halide dispersing agent, adding acid to reduce the pH to 4-5.5 whereby grains of silver-halide enveloped by the dispersing agent and the resin form, separating the liquid therefrom, and redispersing in water at a pH above 6.5

2. A method of preparing acid coagulable silver-halide dispersions of low water soluble salt content which comprises preparing silver-halide in an aqueous solution of gelatin, mixing therewith $\frac{1}{2}$ -1 part of phenoxyacetic acid-formalde-

hyde resin in the form of its alkali metal salt, per part of gelatin, adding aqueous acetic acid to reduce the pH to 4-5.5 whereby coagulation of the gelatin-resin-silver-halide system occurs, allowing the grains so formed to settle and removing the liquid therefrom, and then redispersing the silver-halide grains in an aqueous liquid having a pH of 6.5.

3. A method of preparing washed silver-halide emulsions which comprises preparing silver-halide in an aqueous solution of a silver-halide dispersing agent, mixing therewith $\frac{1}{3}$ -1 part of an alkali-soluble, acid-insoluble organic resin containing carboxyl groups, per part of dispersing agent, reducing the pH to 4-5.5 whereby grains of silver-halide enveloped by the dispersing agent and the resin are obtained, allowing the grains to settle and decanting the liquid therefrom and then dispersing the silver-halide grains in an aqueous solution of a protective colloid whereby a silver-halide photographic emulsion substantially free of water soluble salts is obtained.

4. A method of preparing acid coagulable silver halide dispersions of low water soluble salt content which comprises preparing silver halide in an aqueous solution of gelatin, mixing therewith $\frac{1}{3}$ -1 part of salicylic acid-formaldehyde resin in the form of its alkali metal salt per part of gelatin, adding acid to reduce the pH to 4-5.5 whereby coagulation of the gelatin-resin-silver halide system occurs, allowing the grains so formed to settle, and removing the liquid therefrom and then redispersing the silver halide

grains in an aqueous liquid having a pH of at least 6.5.

5. A method of preparing acid coagulable silver halide dispersions of low water soluble salt content which comprises preparing silver halide in an aqueous solution of gelatin, mixing therewith $\frac{1}{3}$ -1 part of glycerol-phthalic anhydride resin in the form of its alkali metal salt per part of gelatin, adding acid to reduce the pH to 4-5.5 whereby coagulation of the gelatin-resin-silver halide system occurs allowing the grains so formed to settle, and removing the liquid therefrom and then redispersing the silver halide grains in an aqueous liquid having a pH of at least 6.5.

EDWARD C. YACKEL.

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