

UNITED STATES PATENT OFFICE

2,599,494

PHOTOGRAPHIC EMULSIONS

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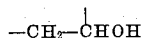
9 Claims. (Cl. 95—7)

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This invention is concerned with photography and, more particularly, with the preparation of photographic emulsions. Still more particularly it is concerned with a process of washing light-sensitive hydroxyl polymer emulsions.

Gelatin has been used as the binding agent for silver halide particles in most of the photographic films and printing papers manufactured during the last decade. Since gelatin is an excellent protective colloid which forms strong, hard, thin films and the particle size of the silver halide grains in the gelatin binder can be controlled, it has many advantages. Gelatin also serves as a source of certain sensitizing materials that are used in obtaining beneficial effects of speed and contrast. However, gelatin has a number of disadvantages which place restrictions upon its use. These disadvantages include (1) a softening action that occurs during processing in warm water and (2) a bacterial decomposition that occurs when stored under hot, humid conditions. Because of these undesirable properties of gelatin, several types of substitutes have been suggested.

Among the proposed gelatin substitutes for this purpose are included the several types of synthetic hydrophilic hydroxyl polymers which contain a plurality of recurring intralinear



groups, including polyvinyl alcohol, partially hydrolyzed polyvinyl acetate and their ethers and acetals, and copolymers with low molecular weight unsaturated compounds, e. g., ethylene. The manufacture of light-sensitive silver halide emulsions containing these hydrophilic synthetic hydroxyl polymers on a commercial scale has presented difficulties in uniformly removing the water-soluble salts formed during precipitation of the silver halide particles. This is because the above-mentioned water-permeable or hydrophilic colloids do not readily form thermally reversible gels. Such salts can be easily removed from gelatin emulsions by gelling the emulsions, shredding the gelled emulsion, and washing the shreds with water to a salt content which gives optimum development of photographic properties during the subsequent digestion process.

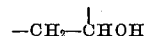
Photographic silver halide emulsions containing non-gelling, hydrophilic hydroxyl polymer colloids of the above type cannot be alternately set or gelled and melted by slight temperature changes like gelatin and, therefore, require special treatment to convert them into suitable form for washing. Agglutination of such emulsions

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by means of sodium sulfate solutions, acetone, etc., have been proposed but some difficulty is encountered during the washing and re-solution of the washed emulsion. The coagulated hydrophilic colloid may tend to peptize in the wash water or tough, rubbery masses may be formed that give slow and uneven washing. Moreover, when using such agglutination procedures, it is difficult to secure proper adjustment of photographic speed and contrast and the final emulsion is likely to contain agglutinates that give a grainy film. In addition, the presence of portions of unwashed emulsion tends to give insoluble clumps that show up in emulsion coatings, being especially objectionable in thin emulsion layers.

An object of this invention is to provide light-sensitive silver halide emulsions that are substantially free from water-soluble salts and contain synthetic hydroxyl polymer colloid binding agents. A further object is to provide a practical method of washing silver halide emulsions having such binding agents.

The present invention comprises precipitating light-sensitive silver halides in a hydrophilic hydroxyl polymer containing a plurality of recurring



groups, coagulating the resulting emulsion in the form of continuous filaments by spinning the silver halide-containing emulsion into a coagulating bath containing an agglutinating agent, collecting the resulting filaments, and washing the filaments.

In the preferred mode of operation, the light-sensitive silver halide particles are precipitated in a fluid mixture of the synthetic, hydrophilic hydroxyl polymer by mixing a solution of a water-soluble halide, such as ammonium bromide, with a solution of a water-soluble silver salt, such as silver nitrate, in the presence of the hydrophilic hydroxyl polymer. The resulting emulsion may be ripened in this form by the procedures used for gelatin emulsion and those described in United States Patent 2,397,866. The emulsion is then coagulated by spinning through a small orifice, such as is used in the formation of filaments for textile use, e. g., rayon, nylon, etc., into a coagulating bath containing agglutinating agents, e. g., acetone, sodium sulfate, and mixtures of such compounds. The continuous filaments containing the light-sensitive silver halide particles are then collected and washed with water to lower the concentration of soluble salts and thereby to promote the desired photographic characteristics. The washed filaments

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are then redissolved by warming in water preferably containing a small amount of ethyl alcohol. The washed emulsion is then digested either in this form or after the addition of extra hydroxyl polymer binder and sensitizing dyes, and the emulsion coated on a support after the customary treatment with color sensitizers and adjustment of viscosity. The above operations are, of course, carried out in the absence of actinic light. The film is dried, exposed to an object, and the latent image developed and fixed in the customary manner.

The invention will be further illustrated by the following examples. The parts are by weight unless otherwise indicated. Wherever required, operations are carried out in the absence of actinic radiations.

EXAMPLE I

The following solutions were prepared at room temperature:

Solution A

70 cc. 3 N AgNO₃

42 cc. 20% aqueous NH₄OH

Solution B

74 cc. 3 N NH₄Br

12 cc. 0.5 N KI

26 cc. water

Solution C

14 grams completely hydrolyzed ethylene/vinyl acetate copolymer having a mol ratio of ethylene to vinyl acetate of 1:28

112 grams water

14 grams ethanol

The ethylene/vinyl acetate copolymer was prepared as described in Example V of Hanford and Roland, Serial Number 466,116 filed June 6, 1942, now abandoned, and the copolymer was hydrolyzed according to the method described in Example XI of United States Patent 2,386,347.

An emulsion containing precipitated silver halide particles was prepared by simultaneous addition at room temperature of Solutions A and B to Solution C at a uniform rate over a period of ten minutes with continuous stirring. The emulsion was then spun into a 20% aqueous sodium sulfate solution using a five hole 3.5 mil spinneret, the silver halide-containing emulsion being forced through the spinneret by an eight foot hydrostatic head. The material coming through the spinneret coalesced to unite the material from the five holes as a single filament which was then drawn slowly through the bath until sufficient mechanical strength was developed to permit stretching the filament approximately 300% in the bath. The stretched filament was wound on a bobbin to a thickness of one-fourth inch and washed in running water. The silver halide-containing filaments on the bobbin were then removed and redissolved in 10% alcohol. One hundred and forty grams (140) of additional copolymer solution (C) was added. The emulsion was digested and coated on a paper support. A sensitometric test showed that the sensitive emulsion had satisfactory photographic properties including fog, speed, contrast, and top density.

EXAMPLE II

The following solutions were prepared:

Solution A

500 cc. 3 N AgNO₃

300 cc. 20% aqueous NH₄OH

600 cc. water

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Solution B

600 grams completely hydrolyzed ethylene/vinyl acetate copolymer solution of the same composition as Solution C of Example I

510 cc. 3 N NH₄Br

420 cc. water

Solution A was brought to 95° F. and Solution B to 112° F. and precipitation of the emulsion was made under non-actinic conditions by adding Solution A to Solution B, with stirring, over a period of three minutes. The precipitated emulsion containing light-sensitive silver halide was placed in a pressure vessel and forced under 15 lbs. pressure through a spinneret of the type used in Example I into acetone. The agglutinated filaments emerging from the spinneret face were allowed to collect in an open-mesh basket immersed in the acetone coagulation bath and were then washed by dipping into water. The light-sensitive filaments were given eight successive washings in fresh water, allowing ten minutes contact with each wash water before draining. The washed filaments were redissolved by addition of 1130 grams of completely hydrolyzed ethylene/vinyl acetate copolymer solution of the same composition as Solution C of Example I, the emulsion being heated 15 minutes at 65° C. to effect solution. The conductivity of the emulsion at this point was 500 micromhos. The emulsion was then digested and finished in the same manner as the emulsion of Example I.

EXAMPLE III

A magenta color-forming emulsion was prepared using as the protective colloid the polyvinyl acetal of m-[p-(5-ethylcarbonato-3-methyl-5-pyrazolyl)benzamido] benzaldehyde described in Example III of Martin, Serial Number 682,137 filed July 8, 1946, now Patent No. 2,476,988 of July 26, 1949. The polymer was dissolved by adding 150 cc. absolute alcohol and six drops of 10% aqueous potassium hydroxide in 400 cc. of water to 30 grams of the polymer. To prepare the emulsion, 100 grams of this polymer solution was mixed with 20 cc. absolute alcohol and the following two solutions added separately and simultaneously over a period of 15 minutes with constant stirring.

Solution A

29 cc. 3 N AgNO₃

20 cc. 20% aqueous NH₄OH

7 cc. water

Solution B

31 cc. 3 N NH₄Br

2 cc. 0.5 N KI

32 cc. water

After precipitation of the silver halide particles, the emulsion was added as a thin stream to a 1000 cc. volume of acetone being stirred with a constant swirling action. The emulsion was added at the outer edge of the acetone agglutinating mixture and the coagulated filaments of light-sensitive emulsion were collected in the center of the coagulation bath. The coagulated filaments were removed and washed in the same manner as that described in Example I. The emulsion was finished by addition of 100 grams of the polymer solution previously described in this example, and digested. It was coated on film base and exposed to light through a step wedge. Development for ten minutes at 20° C. in a p-aminodiethylaniline developer

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(2.5 grams p-aminodiethylaniline HCl, 25 grams $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, two grams KBr, ten grams Na_2SO_3 in 1000 cc. of water), followed by bleaching and fixation in hypo gave a uniform magenta image of good contrast.

EXAMPLE IV

Precipitation of silver halide particles in a fluid synthetic hydroxyl polymer emulsion was made as in Example I, the emulsion placed in a pressure vessel and spun through a spinneret into the bottom of a tank at a six foot depth of 20% aqueous sodium sulfate solution. The pressure at which the emulsion was spun was adjusted so that buoyant force caused the coagulated emulsion to reach the surface of the salt bath in the form of a continuous filament. The filament was then conducted into a second bath containing 20% aqueous sodium sulfate solution where it was stretched 200% and delivered to a third bath where it was washed with water continuously. The filament was then delivered to a vessel containing 10% aqueous ethanol. When the concentration of silver halide in the 10% aqueous ethanol solution reached the point corresponding to the concentration used in finishing the emulsion in Example I, the resulting mixture was warmed to effect solution and the mixture was finished and coated as in Example I.

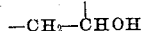
In place of the specific hydrophilic hydroxyl polymers described in the foregoing examples, there may be substituted a large number of other similar hydroxyl polymers. Among such polymers there may be used partially hydrolyzed polyvinyl esters which are usually prepared by incomplete hydrolysis of esters, such as polyvinyl acetate, polyvinyl chloracetate, polyvinyl isobutyrate, etc. Ethers of such hydrolyzed esters can be made by incompletely etherifying the partially hydrolyzed polyvinyl esters. Among such useful ethers are the methyl, ethyl, and benzyl ethers.

Polyvinyl acetals of such partially hydrolyzed polyvinyl esters can be made incomplete acetalization of the partially hydrolyzed polyvinyl esters in the presence of an acetalization catalyst. Suitable polyvinyl acetals include those made from formaldehyde, acetaldehyde, isobutyraldehyde, and benzaldehyde.

Still other useful hydroxyl polymers include polyvinyl alcohols of low, middle, and high viscosity, as well as their ethers and acetals corresponding to those described in the preceding paragraph.

Synthetic hydroxyl polymers having an average molecular weight (number average) of 10,000 to 100,000 are useful but those having an average molecular weight of 25,000 to 50,000 are preferred.

In addition to the hydroxyl polymer color formers described in Example III, there may be substituted various other polymers which contain recurring color former nuclei in addition to the recurring



units. Typical polymers of this type are described in United States Patent 2,310,943, 2,320,422, 2,397,865, 2,415,381 and 2,415,382.

The selection of the agglutinating agent is normally made on the basis of economy and efficiency of precipitation of the emulsion in a suitable form for washing. There are a large number of suitable agglutinating agents but their efficiency varies. A partial list of agents which are useful includes water-soluble electrolytes,

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such as sodium sulfate, aluminum sulfate, sodium chloride, ammonium sulfate, ammonium chloride, barium chloride, sodium bicarbonate, sodium dihydrogen phosphate, disodium hydrogen phosphate, magnesium chloride, calcium chloride, aluminum acetate, zinc chloride, zinc sulfate, and calcium acetate. These agents are also useful as coagulating or flocculating agents. Colored materials and materials which cause fog, such as the chromium, iron, copper, cadmium, and cobalt salts and the like, are normally avoided although they can function as agglutinating agents. The preferred agents of this type are colorless, inorganic, soluble salts which have no pronounced oxidizing or reducing action and similar salts of organic acids containing less than eight carbon atoms. Another class of agglutinating agents suitable for use in this process is the water-soluble organic solvents which are at the same time non-solvents for polyvinyl alcohol. Such materials include acetone, alcohol, methyl acetate, isopropanol, methanol, methyl ethyl ketone. Of these, the lower aliphatic alcohols and ketones are preferred. Agents which combine chemically with the polyvinyl alcohol and cause gelling or cross-linking are not comprehended by the term "agglutinating agent."

The invention, moreover, is not limited to the specific light-sensitive material described in the above-detailed examples. On the contrary, various other simple and mixed silver halides may be used as the light-sensitive materials in like manner. Mixtures of silver bromides, chlorides, and/or iodides can be made by adding mixtures of soluble salts of these halides in like manner. Other useful soluble halides include potassium bromide, potassium iodide, sodium and potassium chlorides and iodides, etc. Other useful silver salts of sufficient solubility include silver sulfamate, silver sulfate, silver citrate, and silver acetate.

The invention is applied to the emulsion after precipitation of the silver halide particles by double decomposition of the silver salt. It is usually advantageous to have a high fraction of the total binder present at this point in order to provide sufficient material for filament formation. It is desirable that the viscosity of the emulsion at this point be as high as possible to facilitate filament formation although the invention has been practiced at ordinary viscosities used in precipitation of the light-sensitive silver halide particles. For many purposes it is desirable to have all of the polymeric binder present before coagulation.

It is important in the practice of this invention that the orifice of the spinneret be sufficiently small so that rapid contact between the agglutinating agent and the entire body of the emerging emulsion stream is quickly attained. For this purpose spinneret holes of the size used in textile spinning, i. e., of the order of 2 to 5 mils may be employed. The mechanical strength of the fiber is attained by use of small spinneret holes followed by coalescence of individual fibers to give a filament that is self-supporting and which can be drawn out in the coagulation bath from 100 to 300% to increase strength. A wide set of conditions is available for conducting the spinning operation. The properties of the emerging filaments of emulsion are considerably different from those formed for textile purposes in that they contain a relatively large amount of light-sensitive silver halide par-

ticles. The weight ratio of imbedded silver halide to the binder in which it is imbedded ranges from 1:1 to 10:1; whereas in textile spinning only relatively small amounts of finely divided particles have been incorporated in the system for the purpose of delustering. The viscosity of the spinning solutions of this case may vary from 5 to 30 and preferably from 10 to 25 centipoises at 25° C.

Furthermore, the viscosity of the light-sensitive emulsions after precipitation of silver halide is lower than that of polymeric solutions used in textile spinning. The light-sensitive emulsion filaments, therefore, set up initially to a relatively weak filament and it is necessary to give special care to their treatment during the early stage after spinning while the large amount of water associated with the silver halide/hydroxyl polymer mixture is being dissipated and mechanical strength developed to permit handling the filaments. The presence of the relatively large amount of silver halide also tends to weaken the filament. It is, therefore, desirable to provide special guides for handling the coagulating filaments as they emerge from the spinneret face. Such guides may take several forms including moving rollers and screens that support the filament and move it forward. This action can also be attained by motion of the water in the coagulation bath by pumping past the spinneret face. Unlike textile spinning art, it is desirable that several filaments stick together to form a single, more uniformly coagulated, and stronger filament than would result from extrusion of a larger filament with care to prevent sticking together. The continuous filament may be relatively large in diameter during the early stage of coagulation but becomes relatively fine (of the order of 0.01 to 0.06 inch in cross section) as it loses water and is drawn out in the coagulation bath to increase mechanical strength. The loss of a large fraction of the original water to the coagulation bath gives a fiber for the washing step which is smaller than that of the ordinary gelatin shreds and which contains considerably less water than the latter.

The spinning process is a continuous one and lends itself to a completely continuous method of making fluid emulsions. The strong filaments may be continuously washed as in the last example or may be "bucket washed" as is ordinarily practiced with the higher water-containing gelatin shreds. All coagulation, spinning, and washing operations are conducted in the absence of light or chemicals that would promote fogging.

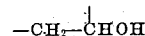
The most important advantage of the invention is that light-sensitive silver halide emulsions containing "non-gelling" polymeric materials may be satisfactorily washed. The uniform structure of the coagulated silver halide-containing filament makes it possible to wash all parts of the emulsion rapidly and uniformly. The final emulsions have all the advantages of uniform washing, including high speed, high contrast, high top density, with low fog.

As many widely different embodiments of this invention can be made without departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited except as defined by the claims.

What is claimed is:

1. The process which comprises precipitating light-sensitive silver halides in a fluid mixture of

a synthetic hydrophilic hydroxyl polymer which contains a plurality of recurring intralinear



groups, extruding the resulting emulsion through a plurality of orifices having a diameter from 2 to 5 mils into a coagulating bath, coalescing the filaments into a fiber, stretching the fiber 100 to 300% of its original length in said bath, removing the stretched fiber and washing the latter with water to remove the water-soluble crystalloidal compounds.

2. The process which comprises precipitating light-sensitive silver halides in an aqueous solution having a viscosity of 5 to 30 centipoises at 25° C. of a synthetic hydrophilic hydroxyl polymer which contains a plurality of recurring intralinear



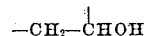
groups in such amount that the weight ratio of silver halide to hydroxyl polymer is from 1:1 to 10:1, extruding the resulting emulsion through a plurality of orifices having a diameter from 2 to 5 mils directly into a coagulating bath, coalescing the filaments into a fiber, stretching the fiber 100 to 300% of its original length in said bath, removing the stretched fiber and washing the latter with water to remove the water-soluble crystalloidal compounds.

3. A process as set forth in claim 2 wherein said hydroxyl polymer is polyvinyl alcohol having an average molecular weight of 10,000 to 100,000.

4. A process as set forth in claim 2 wherein said hydroxyl polymer is a hydrolyzed ethylene/vinyl acetate copolymer.

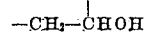
5. A process as set forth in claim 2 wherein said hydroxyl polymer contains recurring color former nuclei.

6. The process which comprises precipitating light-sensitive silver halides in an aqueous solution having a viscosity of 5 to 30 centipoises at 25° C. of a synthetic hydrophilic hydroxyl polymer which contains a plurality of recurring intralinear



groups having a molecular weight of 10,000 to 100,000, in such amount that the weight ratio of silver halide to hydroxyl polymer is from 1:1 to 10:1, extruding the resulting emulsion through a plurality of orifices having a diameter from 2 to 5 mils directly into a coagulating bath, coalescing the filaments into a fiber, stretching the fiber 100 to 300% of its original length in said bath, removing the stretched fiber and washing the latter with water to remove the water-soluble crystalloidal compounds.

7. The process which comprises precipitating light-sensitive silver halides in an aqueous solution having a viscosity of 5 to 30 centipoises at 25° C. of a synthetic hydrophilic hydroxyl polymer which contains a plurality of recurring intralinear

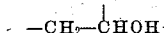


groups in such amount that the weight ratio of silver halide to hydroxyl polymer is from 1:1 to 10:1, extruding the resulting emulsion through a plurality of orifices having a diameter from 2 to 5 mils directly into a coagulating bath, coalescing the filaments into a fiber, stretching the fiber 100 to 300% of its original length in said

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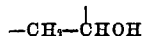
bath, removing the stretched fiber and washing the latter with water to remove the water-soluble crystalloidal compounds and redissolving the washed fiber in water containing a small amount of ethyl alcohol.

8. The process which comprises precipitating light-sensitive silver halides in an aqueous solution having a viscosity of 5 to 30 centipoises at 25° C. of a synthetic hydrophilic hydroxyl polymer which contains a plurality of recurring intralinear



groups in such amount that the weight ratio of silver halide to hydroxy polymer is from 1:1 to 10:1, extruding the resulting emulsion through a plurality of orifices having a diameter from 2 to 5 mils directly into a coagulating bath containing sodium sulfate, coalescing the filaments into a fiber, stretching the fiber 100 to 300% of its original length in said bath, removing the stretched fiber and washing the latter with water to remove the water-soluble crystalloidal compounds.

9. The process which comprises precipitating light-sensitive silver halides in an aqueous solution having a viscosity of 5 to 30 centipoises at 25° C. of a synthetic hydrophilic hydroxyl polymer which contains a plurality of recurring intralinear



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groups in such amount that the weight ratio of silver halide to hydroxyl polymer is from 1:1 to 10:1, extruding the resulting emulsion through a plurality of orifices having a diameter from 2 to 5 mils directly into a coagulating bath containing acetone, coalescing the filaments into a fiber, stretching the fiber 100 to 300% of its original length in said bath, removing the stretched fiber and washing the latter with water to remove the water-soluble crystalloidal compounds.

CLIFFORD K. SLOAN.

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