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1

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## PREPARATION OF PHOTOGRAPHIC EMULSIONS

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This invention relates to photographic silver halide emulsions and more particularly to the preparation of these emulsions.

In the most common method of preparing silver halide emulsions in gelatin the light-sensitive silver salt is formed by reaction of an aqueous solution of a water-soluble halide such as potassium bromide with an aqueous solution of a water-soluble silver salt such as silver nitrate. The gelatin may be dissolved in either or both of the solutions or in a separate solution. After the silver halide is formed the dispersion thereof may be digested or treated in some other manner to impart the desired characteristics. To refine the silver halide dispersion it is first chilled and allowed to set or gel. The gel thus formed is noodled or otherwise comminuted and the water soluble salts present therein are dialyzed out with water having a low temperature. After the salts have been removed and the water is drawn off, the washed emulsion may then be melted by warming and gelatin or some other chemicals may be added to condition the silver halide grains thus obtained.

This process has the great disadvantage that the solidification, noodle formation and washing take a long time. Furthermore, they must be done in the presence of an amount of binding agent which cannot be reduced at will. Indeed, a concentration of at least 4% of binding agent is necessary for solidification and noodle-formation. In some cases, for instance in the preparation of photographic emulsions to be used in X-ray photography, a relatively large amount of light-sensitive salt should be present per unit surface. Such emulsions can be concentrated by evaporating off the water present, the proportion of binding agent to light-sensitive salt, however, remaining unaltered. Consequently, a more concentrated emulsion is only obtained at the expense of a high viscosity, which can hinder the coating of the emulsion, so that instead of concentrating the emulsion too far, it has been preferred to superpose several emulsions on each other to obtain the desired silver salt content per unit surface.

It is also known that solidification and noodle formation may be avoided if, after forming the light-sensitive salt in a solution of a dispersing agent, the latter is caused to precipitate either by addition of a sufficient quantity of liquid in which the dispersing agent is insoluble, or by coagulation, which is effected by adding a salt such as a soluble salt of lead, titanium, thorium, zirconium, ammonium, barium, calcium, sodium or zinc. By precipitation or coagulation in this way, the dispersing agent precipitates together with the light-sensitive silver salt, and a part of the undesired by-products formed. The precipitate may be freed from the latter by washing, but this is difficult and takes up much time, the precipitate being fibrous and sticky.

It is further known that the emulsion can be washed more easily if the light-sensitive silver salt is formed in the absence of a dispersing agent. The light-sensitive salt so obtained can also be washed easily. This technique, however, has the disadvantage that the grains formed in the absence of a dispersing agent very easily aggregate to form

2

clumps of grains which are very difficult to re-disperse to form a homogeneous emulsion without introducing fog.

When pouring an aqueous gelatin solution of a concentration not less than 2% into an organic liquid in which gelatin is insoluble, or into an aqueous solution of a coagulating agent such as sodium sulphate, the gelatin precipitates, but always in such a form that it cannot be filtered off. The greater the concentration of gelatin, the more sticky the precipitate, and at a concentration of 10% of gelatin a rubbery precipitate is obtained.

On the other hand, if the concentration of gelatin is smaller than 2%, the solution becomes turbid and, after standing for a long time, a sticky deposit is formed. At a concentration of 1%, it takes 12 hours for the gelatin deposit to settle out. At lower concentrations one merely gets a small deposit on the walls of the vessel after standing for a much longer time.

When, starting from a silver nitrate solution and an alkali halide, a light-sensitive silver salt is formed in the presence of aqueous gelatin of a concentration not less than 3% and the solution is poured into acetone or an aqueous sodium sulphate solution, the gelatin precipitates in the same form as when no silver salt is present, and the silver salt formed co-precipitates. This precipitate is, as mentioned above, sticky and difficult to wash.

One object of our invention is to provide a method for preparing photographic light-sensitive silver halide emulsions whereby the silver halide dispersion is precipitated in a powdery and very easily washable form.

Another object of our invention is to provide a method for washing the light-sensitive silver halide precipitate of which the tendency to form a sticky mass is avoided.

A further object of our invention is to provide a simple method of freeing the silver halide photographic emulsion from undesired water-soluble by-products.

Further objects will appear from the following description.

We have found that a powdery and very easily washable precipitate can be obtained, which is easily re-dispersed in water, if, by starting from a silver nitrate solution, silver chloride, silver chlorobromide, silver bromoiodide or silver chloroiodide is formed in the presence of a very small amount of gelatin, and the silver salt formed is caused to precipitate by pouring the solution into an organic liquid or a mixture of organic liquids which are miscible with water. The amount of gelatin used for the preparation of the emulsions according to the invention may vary from substantially 2 to 25 g. per 100 g. silver nitrate, depending on the grain size of the emulsion, and the concentration (by weight) of gelatin, before precipitating the emulsion, must not exceed substantially 3% of the water present. A concentration of gelatin of 2% is preferred. The organic liquids which may be used include methyl acetate, ethyl acetate, ethanol, methanol, acetone and their mixtures, although other organic liquids which are miscible with water may be used. For example, in case of acid or neutral emulsions, the precipitating liquid may be acetone, or 100% ethanol, or a mixture of these in any proportion. The quantity of organic liquid is preferably taken in the same order of size as the quantity of silver halide gelatin dispersion although even with rather considerable deviations of this quantity the precipitation still occurs successfully. Acetone, ethanol and their mixtures can also be used for precipitating ammoniacal (alkaline) emulsions, but in this case the quantity of solvent is more critical so that the optimum quantity which must be determined empirically and which usually does not deviate more than 10% of the quantity of dispersion cannot so easily be found. This difficulty can be avoided by neutralizing the ammoniacal (alkaline) emulsions or by acidifying before pouring out into the precipitating liquid.

It is believed that the precipitate formed consists of

silver halide crystals, each enclosed in a thin envelop of gelatin so that the crystals remain discrete.

By proceeding in accordance with this invention, a precipitate quite different from the hereinbefore described sticky gelatin precipitate is obtained. It segregates immediately, so that even with an extremely small concentration of gelatin, a powdery precipitate generally settles out onto the bottom of the containing vessel within about  $\frac{1}{4}$  hour. The precipitate obtained is finely divided, so that it can be washed easily and rapidly with a mixture of water and an organic liquid in which the gelatin is insoluble. After washing, the precipitate may be redispersed in water very easily by gentle warming, and after this the desired amount of binding agent is added.

It will be appreciated that the final proportion of binding agent to light-sensitive salt can be regulated at will, so that emulsions with a very high quantity of light-sensitive salt per unit area can be prepared without increasing the gelatin content, and that less viscous silver salt emulsions can be used to coat a great amount of silver salt on a relatively small surface. The provision of emulsions with easily regulable concentrations of silver salt and gelatin is also particularly beneficial in connection with special coating techniques such as, for instance, coating with an airknife.

After establishing the desired grain distribution of the silver halide by physical ripening in the dilute gelatin solution and freeing the emulsion from the excess of soluble salts by the method of the present invention, the light-sensitivity of the silver halide crystals may be increased by chemical sensitization. The chemical sensitizers may also be added at the precipitation stage of the silver halide or during the Ostwald ripening period, for example when a naturally active gelatin is used as silver halide binder.

It is well known to sensitize emulsions chemically with so-called sulphur sensitizers, which are compounds apparently forming silver sulphide nuclei, or with compounds apparently forming silver nuclei, or with compounds of gold or other heavy metals such as palladium and platinum. In order to sensitize chemically with sulphur sensitizers, the emulsion may be digested with naturally active gelatin, or sulphur compounds such as allyl isothiocyanate, allylthiourea, sodium thiosulphate or potassium selenocyanide may be added.

The emulsions may also be sensitized chemically with compounds apparently forming silver nuclei, for example stannous salts, or imino-amino-methane sulphonic acid compounds such as those described in U.S. patent application Serial No. 581,315.

The emulsions may also be treated in a known manner with compounds of gold or other heavy metals such as ruthenium, rhodium, osmium, palladium, iridium, and platinum, all of which belong to group VIII of the periodic table of elements and have an atomic weight greater than 100.

Surprisingly, it has been discovered that the process of preparing an emulsion according to the present invention has many advantages over the known methods as regards the sensitization with such compounds.

Thus, although the speed-increasing properties of gold compounds have been known for some 30 years (Fr. Kropff, Photographische Industrie 23 (1925) 1145), and such compounds have been widely used for enhancing the sensitivity of many gelatino-silverhalide emulsions, the chemical sensitization of such emulsions by compounds of the heavy metals belonging to group VIII of the periodic table such as platinum and palladium has hitherto not found general application.

Probably this fact may be brought into relation with the difference between the gold compounds and the compounds of other heavy metals such as palladium and platinum with respect to their sensitizing properties in the presence of gelatin. As described by P. Faelens, Science

et Industries Photographiques 27 (1956), 4/7 and 121/122, this difference should result from the respective thermo-reversibility and -irreversibility of the inhibiting action exerted by the gelatin. Thus, although the inhibited sensitizing power of the gold compounds may partially be regenerated by digestion at 40-50° C., the reduced sensitizing power of the compounds of other heavy metals, e.g. platinum and palladium, should hardly be influenced by such a thermal process. On the contrary, 10 in the absence of gelatin or other protein binder for the silver halide, high speed increases may easily be obtained by adding even small amounts of the compounds of heavy metals such as palladium and platinum to the emulsion. By contrast with the addition of gold compounds under 15 the same conditions, the digestion at elevated temperature is no longer necessary for obtaining highly sensitive emulsions, and the quantities to be added are much smaller than in the presence of gelatin. The higher the gelatin concentration in the emulsion, the more this inhibiting action is pronounced.

Thus, the process of emulsion preparation according to the present invention is particularly useful in that it provides a practical and economical method of preparing emulsions, without employing the relatively highly concentrated gelatin solutions as commonly used heretofore for the peptization of the silver halide, so that compounds of gold or of heavy metals belonging to group VIII of the periodic table may be used with advantage as speed-increasing agents.

30 In carrying out the chemical sensitization as indicated above, the heavy metal compounds may be added to the re-suspended silver halide-gelatin precipitate after removing the excess of water-soluble salts but before the addition of the greater amount of gelatin which is necessary for casting the light-sensitive layer.

In the preparation of emulsions according to the present invention, ingredients such as, for example, optical sensitizing dyes, stabilizers, anti-fogging agents, color couplers, hardening agents and wetting agents can be 40 added to the emulsion in a manner known to those skilled in the art.

Our invention will be further illustrated, but is not intended to be limited, by the following examples wherein the parts stated are parts by weight, unless otherwise indicated.

45

#### Example 1

105 parts of silver nitrate, dissolved in 975 parts of distilled water, are added in the course of 1 minute, whilst stirring, to a solution of 90 parts of potassium bromide, 2.5 parts of potassium iodide and 15 parts of gelatin in 450 parts of water. Whilst mixing, the solutions are kept at 40° C. The resulting emulsion is digested for 10 minutes at 45° C. and then poured immediately into 1500 parts of acetone whilst stirring. A fine 55 powder precipitates immediately.

The clear supernatant liquid is decanted, and the fine powdery precipitate is repeatedly washed with a mixture of 62% acetone and 40% water. After washing, the powder is redispersed in 900 parts of water, and 65 parts 60 of gelatin are added for chemical ripening.

The emulsion is applied to a cellulose-ester support and gives a fogless photographic material.

#### Example 2

65 25 parts of silver nitrate, dissolved in 250 parts of distilled water, are added slowly whilst stirring, to a solution of 20 parts of ammonium bromide and 2.5 parts of gelatin in 110 parts of distilled water. Whilst mixing, the solutions are kept at 45° C. The emulsion 70 formed is ripened for 15 minutes at 45° C., and then poured immediately into 500 parts of a concentrated sodium sulphate solution. A fine powder precipitates.

The clear supernatant liquid is decanted and the fine powdery precipitate is repeatedly washed with cold water at about 4° C., after which it is redispersed in 450

75

parts of water. Next, 30 parts of gelatin are added for chemical ripening. The emulsion thus obtained is applied to a cellulose ester support and gives a fogless material.

*Example 3*

100 parts of silver nitrate, dissolved in 90 parts of concentrated ammonium hydroxide, and 85 parts of distilled water are added in the course of a few seconds, whilst thoroughly stirring, to a solution of 90 parts of potassium bromide, 5 parts of potassium iodide and 10 parts of gelatin in 1400 parts of distilled water. A further 125 parts of potassium bromide dissolved in 200 parts of distilled water are added and, within a few minutes, 100 parts of silver nitrate dissolved in 90 parts of concentrated ammonium hydroxide and 85 parts of distilled water are incorporated. The emulsion is ripened for 10 minutes and then poured immediately into a mixture of 2000 parts of acetone and 1000 parts of ethanol, whilst stirring. A fine powdery precipitate is obtained. It is repeatedly washed with a mixture of acetone and water in the proportion 6:4 and is in this way easily freed from the water-soluble by-product salts, and is likewise easily re-dispersed in 3000 parts of water. Next, 250 parts of active gelatin are added for chemical ripening at 45° C. The emulsion thus obtained is highly sensitive and perfectly fogless.

*Example 4*

100 parts of silver nitrate dissolved in 550 parts of distilled water and 45 parts of sodium chloride dissolved in 430 parts of distilled water are simultaneously added to a solution of 12 parts of inert gelatin in 750 parts of distilled water in the absence of actinic light, whilst stirring, in the course of 1 minute.

After 5 minutes stirring at 50° C., the emulsion so obtained is poured into 1800 parts of acetone. A very fine powder is obtained which slowly deposits and which can easily be washed with a mixture of water and acetone in the proportion 6:4. Washing is repeated three times, decanting the supernatant liquid after each time. The powdery precipitate is then re-dispersed in 600 parts of distilled water and the grains chemically ripened with a very diluted aqueous gold chloride solution at 35 to 40° C. When the optimum sensitivity is attained, 55 parts of inert gelatin are added to the emulsion whilst slightly heating and stirring to complete dissolution. The sensitive emulsion so obtained is coated on a cellulose triacetate support.

*Example 5*

50 parts of silver nitrate dissolved in 40 parts of distilled water and 42 parts of concentrated ammonium hydroxide are simultaneously added to a solution of 115 parts of potassium bromide in 285 parts of distilled water wherein 12 parts of photographically active gelatin are dissolved. Immediately thereafter, 55 parts of potassium bromide dissolved in 150 parts of distilled water are added. Next, 112 parts of silver nitrate dissolved in 90 parts of distilled water and 95 parts of concentrated ammonium hydroxide are dropwise added within a period of 10 minutes. The admixture of the solutions is carried out in the absence of actinic light, and whilst thoroughly stirring. The temperature of the solutions amounts to 40° C. After complete addition, the mixture is allowed to digest for 5 minutes whilst stirring. Immediately thereafter it is poured into 1200 parts of acetone. A fine powder precipitates. The supernatant liquid is decanted. The precipitate is re-dispersed twice in 200 parts of distilled water and re-precipitated in 180

parts of acetone. In this way the salts, by-products on the formation of silver bromide as well as the excess of potassium bromide are removed. After the last decantation, the precipitate is re-dispersed in 200 parts of distilled

5 water and 60 parts of photographically active gelatin dissolved in 400 parts of distilled water. The mixture is stirred at 45° C. until the mass has become completely homogeneous. Next, it is diluted with distilled water until 1000 parts. Chemical ripening occurs at 50-52° C.  
 10 10 After addition of 5 cm.<sup>3</sup> of a 10% aqueous polyethylene glycol monostearate solution per kg. emulsion, the finished emulsion is applied to a cellulose triacetate support.

We claim:

15 1. A process of preparing a powdery and very easily washable light-sensitive silver halide precipitate, comprising mixing silver nitrate, at least a single water-soluble halide, and an aqueous solution of gelatin, the gelatin being used in a ratio of about 2 to 25 grams per 100  
 20 20 grams silver nitrate, the amount of water being such that the quantity of gelatin does not exceed about 3% by weight of the water present, allowing the aqueous dispersion formed to ripen, and mixing the ripened dispersion into an approximately equal amount of a precipitating organic liquid, thereby obtaining the desired precipitate in powdery form, said organic liquid being selected from a group consisting of methyl acetate, ethyl acetate, ethanol, methanol, acetone, and their mixtures.  
 25 2. In the process according to claim 1, said first named  
 30 30 mixing being done by mixing 105 grams silver nitrate, 90 grams potassium bromide, 2.5 grams potassium iodide, and 15 grams gelatin in 1425 grams water, and said second named mixing being done by mixing the silver bromo-iodide dispersion obtained into 1500 grams acetone.  
 35 3. In the process according to claim 1, said first named mixing being done by mixing 200 grams silver nitrate, 215 grams potassium bromide, 5 grams potassium iodide, and 10 grams gelatin in 1770 grams water and 180 grams  
 40 40 concentrated ammonium hydroxide, and said second named mixing being done by mixing the silver bromo-iodide dispersion obtained into 2000 grams acetone and 1000 grams ethanol.  
 45 4. In the process according to claim 1, said first named mixing being done by mixing 100 grams silver nitrate, 45 grams sodium chloride, and 12 grams gelatin in 1730 grams water, and said second named mixing being done by mixing the silver chloride dispersion obtained into 1800 grams acetone.  
 50 5. In the process according to claim 1, said first named mixing being done by mixing 162 grams silver nitrate, 170 grams potassium bromide, and 12 grams gelatin in 565 grams water and 137 grams concentrated ammonium hydroxide, and said second named mixing being done by mixing the silver bromide dispersion obtained into 1200 grams acetone.

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