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PRODUCTION OF PHOTOGRAPHIC SILVER
HALIDE EMULSIONS FROM GELATIN-
ANION SOAP COMPLEXES

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This invention relates to the production of silver halide photographic emulsions.

When an anion soap is added to an emulsion of silver halide in gelatin, at a low pH value or in the presence of an electrolyte (when the pH value need not necessarily be low), a complex is formed between the gelatin and anion soap and this separates out carrying the silver halide with it.

It has now been discovered that the gelatin/anion soap complexes thus formed, and also analogous complexes formed with a sulphonic acid containing a highly hydrophobic radicle in the anion, are readily dispersible in organic solvents, e. g. methyl alcohol. According to this invention, therefore, photographic emulsions in which the solvent medium is predominantly organic are formed by dispersing in an organic solvent medium a complex formed by precipitating gelatin from its aqueous dispersion containing silver halide in suspension, by means of an anion soap, or by means of a sulphonic acid containing a highly hydrophobic radicle in the anion, the said aqueous dispersion being at a pH value below the isoelectric point of the gelatin, or at a higher pH value and containing an electrolyte. The precipitated complex may contain a small proportion of water and this be included in the organic solvent dispersion.

According to a further feature of the invention, there is included in a photographic emulsion so formed a proportion of another colloid which is soluble in the solvent medium already present in the emulsion, or which is soluble in a solvent medium which is miscible with the solvent medium already present in the emulsion, to form a stable combination.

The gelatin/anion soap complex and analogous complexes formed from sulphonic acids as defined above, containing silver halide, may be prepared by the addition of the anion soap solution to the gelatin silver halide emulsion and allowing the gelatin complex to sediment out. The complexes may be redispersed in the organic solvent medium without washing, but it is preferred to wash the complex to remove unwanted ions. Instead of the anion soap itself, the corresponding free acid may be employed. The technique of maintaining the original aqueous dispersion of the colloid at a low pH value ap-

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pears to be equivalent in effect to the use of the free acid, but the use of the free acid presents the advantage that the resulting complex is not contaminated with the cation of the anion soap. Complexes free from water-soluble salts are found to be more readily dispersible in some organic solvent media.

The invention will be described with particular reference to the use of anion soaps, but it is to be understood that sulphonic acids which, though not true anion soaps, contain a highly hydrophobic anion, can be used analogously.

It has been discovered that for each particular anion soap there is an optimum ratio of the soap to the gelatin which results in a gelatin complex of the highest solubility in organic solvents, and a method is available for determining such optimum ratio in each particular case.

If an anion soap is added in gradually increasing quantity to a gelatin solution at low pH, or at higher pH in the presence of electrolyte, a gelatin/anion soap complex forms and separates out. By measuring the amounts of the anion of the anion soap remaining in the supernatant liquid after the mixture has been allowed to stand for some hours, thus reaching equilibrium, and plotting these quantities as ordinates against the quantities of anion soap added as abscissae, using a logarithmic scale, a curve is obtained showing a straight line rising portion followed by a fall where the complex begins to separate. The curve falls to a minimum value and then rises again. It has been discovered that, generally speaking, this minimum value (referred to as the "inflection point") represents the particular complex having the greatest hydrophobic character and the greatest solubility in organic solvents. The precise position of the inflection point, however, depends on various factors, including the pH and the quantity of electrolyte present, if any.

A curve of this type can be obtained in respect of any particular anion soap which it is desired to use, and it may be said that, as a general proposition, where plain gelatin is concerned, the preferred conditions for obtaining the highest degree of solubility in organic solvents are that the anion of the anion soap used should be as strongly hydrophobic as possible, the pH of the solution should be below the isoelectric point of

the gelatin, the electrolyte concentration in the solution should be as low as possible, and the concentration of the anion soap should be as near the inflexion point as possible. The low pH value enables the use of the free acid of the anion soap. Generally speaking pH values of the order of 2.5 to 3.0 are suitable, but lower values, e. g. as low as 2.0 may be used.

However, where, as in the present invention, the gelatin solution employed is a photographic emulsion, it is not always possible to achieve these conditions owing to other factors involved in the technique of producing satisfactory emulsions. For example, it is generally not desirable to prepare photographic emulsions at a pH value lower than 3. Moreover, it is seldom practical to allow the emulsion to stand with the anion soap over the long period which may be necessary to obtain equilibrium. Accordingly, the preferred procedure is to ascertain the "true" inflexion point using a plain gelatin solution and an anion soap under conditions which approximate as closely as possible to the conditions which will be necessitated for a particular gelatin photographic emulsion, and then to use a quantity of anion soap with such emulsion which corresponds to that portion of the curve which follows the inflexion point, i. e. to use a concentration of anion soap which is that at the inflexion point or slightly greater.

Moreover for emulsion-making it is generally desirable that the precipitated gelatin/anion soap complex should be soluble in water-miscible solvents since the precipitated complex invariably contains water, and it is difficult to remove this water without adversely affecting the quality of the emulsion. To this end it is generally desirable to treat the emulsion at a pH below the isoelectric point of the gelatin and in the presence of as little electrolyte as possible, since these conditions appear to favour the production of complexes soluble in water-miscible solvents. To ensure a low pH value it is preferred to use an emulsion which is at a pH value below the isoelectric point of the gelatin and then to add, either the free acid of the anion soap or the anion soap itself together with sufficient mineral acid to neutralise the cation of the anion soap.

Anion soaps are surface-active compounds in which the reduction in surface tension resultant on their addition to water is due to the anion. The classification of soaps is discussed in the book *Kolloidchemische Grundlagen der Textilveredlung* by Dr. E. Valko, 1937, at pages 519-522, to which reference is made for the meaning of the expression "anion soaps."

Specific classes of compounds falling within this generic expression are as follows:

(a) Soluble salts of long-chain-alkyl carboxylic acids, e. g. soluble salts of fatty acids containing 8 or more carbon atoms, as for example, oleic, ricinoleic, linoleic, stearic and palmitic acids.

These, however, are in general much less satisfactory for use than:

(b) Soluble salts of long-chain-alkyl sulphonic acids.

(c) Soluble salts of sulphated higher fatty alcohols, e. g. soluble salts of fatty alcohol sulphates of which the alkyl group contains at least 8 carbon atoms, as for example the soluble salts of lauryl hydrogen sulphate and oleyl hydrogen sulphate.

(d) Soluble salts of sulphated secondary al-

cohols containing at least 8 carbon atoms in the chain.

(e) Soluble salts of alkylated aromatic sulphonic acids, e. g. soluble salts of alkyl benzene sulphonic acids, of alkyl naphthalene sulphonic acids and of alkylated hydroxy diphenyl sulphonic acids.

(f) Soluble salts of long-chain-alkyl esters of sulphated succinic acid.

Thus, it will be seen that anion soaps containing sulphonic or sulphuric acid groups are preferred to those containing carboxylic acid groups.

The soluble salts may be formed from alkali metals, e. g. sodium and potassium, from ammonia or from amines, e. g. triethanolamine and cyclohexylamine.

The anion soaps may contain amino residues in the anion of the soap as, for example, in the sodium salt of oleoyl amino ethane sulphonic acid which contains a carbonamido ($-\text{NH}.\text{CO}-$) group.

The expression "long-chain-alkyl" is intended to mean at least 8, and preferably at least 12, carbon atoms in the alkyl group.

Very many anion soaps are commercially marketed as detergents and these commercial products may conveniently be employed in the process of this invention. Thus suitable commercial products are the compounds sold under the trade names:

Agral N	Nekal BX
Aresklene 375	Perminal N
Dispersol	Santomer D
Gardinol	Sulphonated Lorol T. A.
Igepon T	Sulphonated Lorol N. H.
Lissapol A	Sulphonated Lorol C. Y.
Lissapol C	Sulphonated Ocenol
Lissatan A	Teepol X
Lohrinol	Tergitol 4
Nekal A	Tergitol 7

Agral N is the sodium salt of an alkyl naphthalene sulphonic acid.

Aresklene 375 is the sodium salt of an alkyl-oxydiphenyl disulphonic acid.

Dispersol is the sodium salt of dinaphthyl methane disulphonic acid.

Gardinol is an alkali metal sodium long-chain-alkyl sulphate of 10 to 18 carbon atoms.

Igepon T is the sodium salt of oleoyl-methylamino-ethane sulphonic acid.

Lissapol A is sodium hexadecyl sulphate.

Lissapol C is sodium hexadecyl sulphate.

Lissatan A is a condensation product of sodium hexadecyl sulphate and formaldehyde.

Lohrinol is a sulphonated fatty acid.

Nekal A, Nekal BX, and Perminal N are sodium salts of alkyl naphthalene sulphonic acids.

Santomer D is the sodium salt of an alkyl benzene sulphonic acid.

Sulphonated Lorol T. A. is triethanolamine dodecyl sulphate.

Sulphonated Lorol N. H. is ammonium dodecyl sulphate.

Sulphonated Lorol C. Y. is cyclohexylamine dodecyl sulphate.

Sulphonated Ocenol is a sulphonated mixture of aliphatic unsaturated alcohols of 16 to 18 carbon atoms predominating in the latter.

Teepol X is a mixture of sodium alkyl sulphates of 10 to 18 carbon atoms.

Tergitol 4 and Tergitol 7 are sodium secondary-alkyl sulphates.

Such commercial detergents and still more the

pure anion soaps contained in them, are much preferred to the ordinary alkali-metal soaps of fatty acids referred to under (a) above. As already indicated, there may be used, instead of the anion soap itself, the free acid derived from such soap.

As indicated above, instead of true anion soaps, certain sulphonic acids of which the anion is highly hydrophobic may be employed. These may be simple acids, for example 2-naphthol-1-sulphonic acid, 1-naphthol-4-sulphonic acid or anthraquinone-2-sulphonic acid, or may be more complex, for example dyestuffs such as Kiton Fast Yellow 3G (Colour Index No. 645) which contains a sulpho-aryl-pyrazolone radicle, and Naphthalene Orange GS (Imperial Chemical Industries Ltd.).

In general it is preferred to form the complex from an aqueous gelatino-silver halide emulsion which has already been washed and digested.

Generally speaking the most suitable organic solvents for dispersing the complexes are those containing hydroxy groups, e. g. methyl and ethyl alcohols, ethylene glycol mono methyl ether, ethyl lactate and diacetone alcohol. Organic solvents not containing hydroxy groups are generally only useful together with some water or some hydroxy solvent, e. g. acetone, methyl ethyl ketone, dioxane, methylene chloride, chloroform and mesityl oxide are preferably used in admixture with water or methyl alcohol. Small quantities of esters, e. g. methyl acetate, butyl acetate, ethers, e. g. diethyl ether, and hydrocarbons, e. g. benzene and toluene, may also be included in the solvent medium. The choice of solvent will depend on the particular nature of the complex. Complexes formed at low pH and containing a relatively low proportion of the anion soap (or corresponding acid) are generally more easily soluble in polar solvents or in solvents containing some water, whilst those formed at higher pH values and containing more anion soap (or corresponding acid) are generally soluble in non-polar solvents, e. g. toluene. The complexes may be swollen in the organic solvent medium and dispersion is usually facilitated by gentle warming.

As already indicated, an important feature of this invention is the formation of photographic emulsions which comprise a gelatin/anion soap complex, containing silver halide, dispersed in an organic solvent medium, together with a proportion of another colloid soluble in such organic solvent medium or in an organic solvent medium miscible therewith. Such other colloids may be, for example, cellulose esters, e. g. cellulose nitrate, cellulose acetate, far-hydrolysed cellulose esters (e. g. cellulose acetate having an acetyl content of 20 to 30%), polyvinyl acetates, polyvinyl acetals, methyl methacrylate polymers and the partial hydrolysis products thereof, alkyd resins, and mixed interpolymers such as the interpolymers of maleic acid or anhydride with styrene or methyl methacrylate.

The following examples illustrate the invention, but are not to be regarded as limiting it in any way:

Example I

500 ccs. of a normal aqueous gelatino silver iodobromide emulsion containing 10% gelatin were melted and diluted to $4\frac{1}{2}$ litres with water. To this was added 100 grams of the commercial anion soap Agral N (essentially an alkyl naphthalene sodium sulphonate) dissolved in 1 litre of water, and this was followed by 40 ccs. of 2N

hydrochloric acid. The gelatin/anion soap complex (containing suspended silver halide) separated as a mass resembling soft gum. It was washed with water, dissolved in 400 cc. warm methyl alcohol and reprecipitated by adding 100 cc. of water. Adhering liquid was then removed from the complex by allowing it to drain, and the complex was then re-dissolved in 400 cc. warm methyl alcohol to form a satisfactory photographic emulsion. Its sensitometric characteristics were substantially the same as those of the original aqueous gelatin emulsion from which it was obtained.

Example II

To a photographic emulsion in methyl alcohol obtained in Example I was added, in turn:

	Cc.
Ethylene glycol mono-methyl ether-----	400
Low viscosity cellulose nitrate (10% solution in methyl alcohol)-----	300
Acetone-----	400

The final emulsion so obtained was stable and suitable for coating by the usual techniques. It was especially suitable, however, for coating by the spray-coating technique. It had a suitable viscosity for this purpose and could be sprayed on to cellulose nitrate lacquered metal without the need for any special substratum or anchoring layer since it adhered strongly to the lacquer coating both in the dry condition and during all stages of processing. The emulsion developed normally, and it was found that the coating was not melted by hot water.

In each of the following Examples III to VI the range of quantities of anion soap employed lie on the portion of the curve, referred to above, which follows the inflexion point as determined under comparable conditions in the absence of the silver halide and allowing the complex to separate until equilibrium conditions are reached.

Example III

A water-washed gelatin silver halide photographic emulsion of high contrast characteristics was digested and stabilised. It was then diluted to a gelatin concentration of 0.67%, it then containing 0.51% suspended silver halide. The pH of the emulsion was then adjusted to 3.0 by the addition of acid.

Portions of the emulsion were then adjusted to a temperature of 50° C. and quantities of various anion soaps at pH 2.2 were added. The optimum quantities were found to be as follows:

Anion Soap	Quantity added per litre of emulsion
	Grams
Dodecyl sodium sulphate-----	2 to 4
Gardinol 30-----	4 to 15
Agral N-----	5 to 10
Perminal N-----	3.5 to 10
Aresklene 375-----	3.5 to 8
Teepol X-----	10 to 30
Sautomerse D-----	2.5 to 5
Aresket 240-----	7.1 to 31.5
Igepon T-----	7 to 15

In each case a precipitate of the silver halide, suspended in a gelatin/anion soap complex, was formed. Ten minutes after the addition of the anion soap the supernatant liquid was removed by decantation. The complex was then washed with water, dispersed in methyl alcohol (100 cc. for the complex from 1 litre of the emulsion),

re-precipitated with water and re-dispersed in methyl alcohol. The resulting dispersion was coated on glass or other convenient support and dried.

The resulting emulsion coatings were of satisfactory photographic quality and could be processed in a developer of the normal constitution, fixed and washed in the usual way.

Example IV

Although in Example III the emulsion used was of low gelatin concentration, it is not necessary to work at such low gelatin concentrations. This example illustrates the preferred conditions for a simple anion soap, Aresket 240, with various dilutions of the emulsion, the general conditions being as in Example III.

Emulsion		Concentration of Aresket 240 per litre of emulsion
Gelatin Concentration	Silver Concentration	
<i>Per Cent</i>	<i>Per Cent</i>	<i>Grams</i>
1.34	1.02	11.3
2.68	2.04	17.7
4.02	3.06	25.2
5.36	4.08	29.0
6.70	5.10	37.8

The complexes thus obtained are readily dispersible in methyl alcohol to form emulsions for coating as in Example II.

Example V

This example illustrates the effect of added electrolyte. An emulsion was prepared as in Example III, except that the pH was adjusted to 7.3 and ammonium nitrate was added to the extent necessary to form a 0.5 Normal solution. The optimum quantities of anion soap were found to be:

Anion Soap	Quantity added per litre of emulsion
	<i>Grams</i>
Teepol X.....	30 to 50
Santomerse D.....	5 to 10

The resulting complexes, containing a substantial amount of adsorbed or absorbed water, were readily dispersible in methyl alcohol to form emulsions suitable for coating as in Example III.

Example VI

This example illustrates the use of a gelatin photographic emulsion of which the gelatin has a high isoelectric point.

500 cc. of an emulsion made with an acid-processed gelatin was diluted to a gelatin concentration of 0.67% when it contained 0.5% of suspended silver halide. Its pH was adjusted to 6.0 and 4 cc. of a 63% solution of Aresket 240 was added, the pH being maintained at 6.0 by further hydrochloric acid addition. The required complex precipitated and was washed and dispersed in methyl alcohol as in Example III.

It will be noted that this complex was formed at the relatively high pH 6.0, but in the absence of added electrolyte. This is only practicable for the reason that the gelatin used had an isoelectric point about pH 7.5. An emulsion made with normal lime-processed gelatin gave no precipitation under these conditions.

Although in the above examples the precipitated complexes have been re-dispersed in methyl

alcohol to form emulsions for coating, other water-miscible solvents may be used, for example ethyl alcohol and ethylene glycol monomethyl ether.

The silver halide emulsions of this inventory may contain any of the usual additions to silver halide emulsions, e. g. optical sensitising dyes, sulphur sensitisers as for instance allyl isothiocyanate, gold salts as described in British Patent No. 570,393 and corresponding United States Patent No. 2,399,083, stabilisers, anti-fogging agents, toning agents and other agents for modifying the speed, contrast, graininess, fog level and image colour of the products.

The invention provides photographic emulsions having a gelatin basis dispersed in organic solvent and the emulsions are therefore of value in a number of special applications. As already indicated they are of particular value for spray coating. Normal gelatin silver halide emulsions present considerable difficulties in spray coating since it is usually necessary to maintain the emulsion warm in the spray-gun to prevent it setting therein. Moreover, the ordinary emulsions will not adhere firmly if sprayed on to lacquered metal sheet. Emulsions may be prepared according to this invention, however, which have little tendency to set in the spray-gun. Moreover, the organic solvent usually has a slight solvent action on lacquered surfaces and thus facilitates adhesion between such surfaces and the emulsion sprayed thereon.

The spray-coating of lacquered metal sheets with photographic emulsion is of particular value in the production of photo-templates. In the commercial application of this process, however, the users generally prefer that the emulsion should be supplied in dry granular condition so that it may be re-dispersed when required to form an emulsion suitable for spraying. The present emulsions are especially suitable in this connection. Emulsions prepared in organic solvent media according to this invention can easily be dried by the well-known expedients of film drying, spray drying, and air drying of the emulsion in the form of a shredded set jelly, since the organic solvent readily evaporates. A further method is to precipitate the emulsion by adding it to water and, after breaking up the precipitate, to air-dry the product. The following specific Example VII illustrates this technique. In this example the emulsion contains a matting agent, though this is not essential.

Example VII

200 grams of a gelatin silver halide emulsion were melted at 100° F. and to this was added 4 grams of "Celite 204" (a commercial form of purified diatomaceous earth) dispersed in 600 cc. water containing 0.4 gm. gelatin. To the product was added 35 cc. of Teepol X and the mixture stirred. 25 cc. of normal hydrochloric acid was then added, the mixture allowed to stand for 15 minutes and the supernatant liquid decanted. The precipitate was washed with 500 cc. water for 2 minutes and the washing liquid decanted. The precipitate was then dissolved in 100 cc. of methyl alcohol at 125° F. and then re-precipitated by adding 75 cc. of distilled water. The precipitate was then re-dissolved in 200 cc. methyl alcohol at 125° F., and 15 grams of cellulose nitrate and 200 cc. of acetone were added.

200 cc. of the resulting emulsion was poured into 1 litre of cold distilled water and stirred. The resulting precipitate was shredded, soaked for 10 minutes in 500 cc. water, and then spread

out to dry. The lumps dried without adhering to one another to any serious extent.

Another useful method of forming dried emulsions from the emulsions in organic solvent prepared according to this invention consists in shredding the set jelly emulsion into water and then air-drying the shreds. This method is illustrated in the following Example VIII.

Example VIII

An emulsion was prepared as in Example VII. It was set to a jelly and shredded by pressing through a perforated plate into water. About 200 cc. of the emulsion was shredded in this way into about 1 litre of cold distilled water, the shreds stirred for about 15 minutes, the water decanted, a further 500 cc. water added, further stirred for 15 minutes, and the shreds then drained and spread out to dry. The shreds did not adhere together during drying. They were, while wet, of the consistency of soft rubber and were easily handled.

The emulsion was readily re-constituted by allowing the shreds to swell in methyl alcohol for 30 minutes and then melting at 125° F.

A dried emulsion suitable for re-constituting in water or aqueous alcohol can be made by a similar method, the cellulose nitrate being omitted. Re-constitution can be effected by soaking in water containing sufficient sodium bicarbonate to neutralise the acid and melting at 120° F. An emulsion suitable for spraying can be made by using 50 grams of the dried emulsion shreds, 2 grams of sodium bicarbonate, 500 cc. of water and 500 cc. of ethyl alcohol (64° O. P.).

The emulsions of this invention, either as originally prepared or as re-constituted after drying, can be used in any process where spray-coating is required. The production of phototemplates has already been mentioned, and another useful application is in the preparation of dials, nameplates and the like on metal or other surfaces. A further application is in the preparation of silk-screen printing surfaces. In this application the emulsion is sprayed on to stretched silk, dried, exposed, developed in a tanning developer and washed in hot water to produce a wash-out relief image. It is a peculiar characteristic of the emulsions of this invention that, though quite insoluble in water when coated, they tend to become soluble when allowed to stand in contact with alkali, as in normal development, though the emulsions are still not soluble in water except at high temperatures. Fixing in an acid fixing bath, however, restores the insolubility of the complex even in hot water. Thus a suitable technique for using the emulsions in the production of silk screen relief images is to develop the exposed image in alkaline pyrocatechol, plunge the silk into hot water and then to fix the wash-out relief image. An alternative technique is to prepare the wash-out relief image on a support from which it may be stripped and to transfer the image to a silk support.

The emulsions of this invention are also of value in colour photography. Thus they may contain dyes or dye-intermediates, e. g. colour-formers which react with the oxidation products of aromatic primary amino developing agents to form quinone-imine or azo-methine dyes, the colour-former being uniformly dispersed in the emulsion. The colour-former, especially where particulate or of very high molecular weight,

may be included in the original emulsion and precipitated with the complex, or it may be added to the final emulsion. Many of the high-molecular weight colour-formers, which are preferred from the standpoint of being non-diffusing in the emulsion, are difficult to disperse in ordinary aqueous gelatin silver halide emulsions, but much more easily dispersed in the organic solvent emulsions of this invention.

The emulsions of this invention are permeable to ordinary alkaline developers, but the degree of permeability depends on the precise constitution of the emulsion. By a suitable selection of an additional colloid, e. g. cellulose nitrate or a hydrophobic acid colloid, emulsions of varying degree of developer-permeability may be made, and accordingly it is possible to build up a multi-layer photographic material for colour photography in which the several layers have different degrees of permeability to ordinary developers and, by adjusting the constitution of the developers, e. g. by adding organic solvents, to develop each of the layers separately. In such a process, by using aromatic primary amino developing agents containing different colour-formers, images in different colours may be formed in the various layers, and by a suitable selection of colour-formers a final true-colour image may be obtained.

Another use to which the emulsions of this invention may be put is in the production of printing paper to be used for printing from wet negatives. As already stated the emulsions of this invention have a good resistance to water, though they are readily developed by ordinary alkaline developing solutions. Paper coated with emulsion according to this invention may be used for printing from wet negatives, though it is usually desirable to employ an emulsion containing a proportion of other colloids, e. g. cellulose nitrate and a methyl methacrylate-methacrylic acid co-polymer. Such emulsions not only have a good resistance to water but also a good resistance to hypo, which may be carried by the wet negative. Advantageously, in the production of wet-printing paper using the emulsions of this invention the emulsion should be supercoated with a layer of a plain gelatin/anion soap complex in organic solvent, as described in our co-pending United States application Serial No. 623,446, filed October 19, 1945, now Patent No. 2,527,262, corresponding to British applications Nos. 21,092/44 and 24,779/44.

What we claim is:

1. A photographic emulsion comprising a dispersion in a predominantly organic solvent medium of a complex of gelatin with an anion soap which is soluble in a solution composed of methyl alcohol, said complex being the essential binding agent for light-sensitive silver halide grains which are dispersed therethrough.
2. A photographic emulsion comprising a dispersion in a predominantly organic solvent medium of a complex of gelatin with an anion soap containing a sulphur acid group which is soluble in a solution composed of methyl alcohol, said complex being the essential binding agent for light-sensitive silver halide grains which are dispersed therethrough.
3. A photographic emulsion comprising a dispersion in a predominantly organic solvent medium of a complex of gelatin with a water-soluble salt of a sulphated higher fatty alcohol which is soluble in a solution composed of methyl alcohol, said complex being the essential binding

agent for light-sensitive silver halide grains which are dispersed therethrough.

4. A photographic emulsion comprising a dispersion in a predominantly organic solvent medium of a complex of gelatin with an anion soap which is soluble in a solution composed of methyl alcohol, said complex being the essential binding agent for light-sensitive silver halide grains which are dispersed therethrough, said emulsion further containing a proportion of another colloid which is soluble in the said solvent medium.

5. A photographic emulsion comprising a dispersion in a predominantly organic solvent medium of a complex of gelatin with a water-soluble salt of a long-chain-alkyl sulphonic acid which is soluble in a solution composed of methyl alcohol, said complex being the essential binding agent for light-sensitive silver halide grains which are dispersed therethrough, said emulsion further containing a proportion of another colloid which is soluble in the said solvent medium.

6. A photographic emulsion comprising a dispersion in a predominantly organic solvent medium of a complex of gelatin with a water-soluble salt of a sulphated higher fatty alcohol which is soluble in a solution composed of methyl alcohol, said complex being the essential binding agent for light-sensitive silver halide grains which are dispersed therethrough, said emulsion further containing a proportion of cellulose nitrate.

7. A photographic emulsion comprising a dispersion in a predominantly organic solvent medium of a complex of gelatin with a water-soluble salt of a long-chain-alkyl sulphonic acid which is soluble in a solution composed of methyl alcohol, said complex being the essential binding agent for light-sensitive silver halide grains which are dispersed therethrough, said emulsion further containing a proportion of cellulose nitrate and a proportion of a hydrophobic acid colloid.

8. A photographic emulsion comprising a dispersion in a predominantly organic solvent medium containing methyl alcohol of a complex of gelatin with an anion soap which is soluble in a solution composed of methyl alcohol, said complex being the essential binding agent for light-sensitive silver halide grains which are dispersed therethrough.

9. A photographic emulsion comprising a dispersion in a predominantly organic solvent medium containing methyl alcohol of a complex of gelatin with a water-soluble salt of a sulphated higher fatty alcohol which is soluble in a solution composed of methyl alcohol, said complex being the essential binding agent for light-sensitive silver halide grains which are dispersed therethrough.

10. A photographic emulsion comprising a dispersion in a predominantly organic solvent medium containing methyl alcohol and acetone of a complex of gelatin with an anion soap which is soluble in a solution composed of methyl alcohol, said complex being the essential binding agent for light-sensitive silver halide grains which are dispersed therethrough, said emulsion further containing a proportion of another colloid which is soluble in the said solvent medium.

11. A method for the production of photographic emulsion in a predominantly organic solvent medium which comprises forming an emulsion of silver halide in an aqueous solution of gelatin, adding to such emulsion an anion soap in a concentration near the inflexion point at a pH below the isoelectric point of the gelatin and

in the presence of a minimum concentration of electrolyte whereby a complex of gelatin and the anion soap is precipitated which is soluble in a solution composed of methyl alcohol and contains the dispersed silver halide and redispersing the said complex with the dispersed silver halide in a predominantly organic solvent medium.

12. A method for the production of photographic emulsion in a predominantly organic solvent containing hydroxyl groups which comprises forming an emulsion of silver halide in an aqueous solution of gelatin, adding to such emulsion an anion soap in a concentration near the inflexion point at a pH below the isoelectric point of the gelatin and in the presence of a minimum concentration of electrolyte whereby a complex of gelatin and the anion soap is precipitated which is soluble in a solution composed of methyl alcohol and contains the dispersed silver halide and redispersing the said complex with the dispersed silver halide in a predominantly organic solvent containing hydroxyl groups.

13. A method for the production of photographic emulsion in a predominantly organic solvent medium which comprises forming an emulsion of silver halide in an aqueous solution of gelatin, adding to such emulsion an anion soap containing a sulphur acid grouping in a concentration near the inflexion point at a pH below the isoelectric point of the gelatin and in the presence of a minimum concentration of electrolyte whereby a complex of gelatin and the anion soap is precipitated which is soluble in a solution composed of methyl alcohol and contains the dispersed silver halide and redispersing the said complex with the dispersed silver halide in a predominantly organic solvent medium.

14. A method for the production of photographic emulsion in a predominantly organic solvent medium which comprises forming an emulsion of silver halide in an aqueous solution of gelatin, adding to such solution at a pH below the isoelectric point of the gelatin an anion soap containing a sulphonic acid grouping, in a concentration near the inflexion point and in the presence of a minimum concentration of electrolyte whereby a complex of gelatin and the anion soap is precipitated which is soluble in a solution composed of methyl alcohol and contains the dispersed silver halide and redispersing said complex with the dispersed silver halide in a predominantly organic solvent medium.

15. A method for the production of photographic emulsion in a predominantly organic solvent medium which comprises forming an emulsion of silver halide in an aqueous solution of gelatin, a water-soluble salt of a long chain alkyl sulphonic acid, in a concentration near the inflexion point at a pH below the isoelectric point of the gelatin and in the presence of a minimum of electrolyte whereby a complex of gelatin and said salt is precipitated which is soluble in a solution composed of methyl alcohol and contains the dispersed silver halide and redispersing said complex with the dispersed silver halide in a predominantly organic solvent medium.

16. A method for the production of photographic emulsion in a predominantly organic solvent medium which comprises forming an emulsion of silver halide in an aqueous solution of gelatin, a water-soluble salt of a sulphated higher fatty alcohol, in a concentration near the inflexion point at a pH below the isoelectric point of the gelatin and in the presence of a minimum of electrolyte whereby a complex of gelatin and

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said salt is precipitated which is soluble in a solution composed of methyl alcohol and contains the dispersed silver halide and redispersing said complex with the dispersed silver halide in a predominantly organic solvent medium.

17. A method for the production of photographic emulsion in a predominantly organic solvent medium which comprises forming an emulsion of silver halide in an aqueous solution of gelatin, a water-soluble salt of a long chain alkyl sulphonic acid, in a concentration near the inflexion point at a pH below the isoelectric point of the gelatin and in the presence of a minimum of electrolyte whereby a complex of gelatin and said salt is precipitated which is soluble in a solution composed of methyl alcohol and contains the dispersed silver halide and redispersing said complex with the dispersed silver halide in a predominantly organic solvent medium, washing said complex with the dispersed silver halide, drying it down to granular form and redispersing it in a predominantly organic solvent medium.

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