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PRODUCTION OF PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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

In the manufacture of photographic gelatino silver halide emulsions, other than those of the print-out types which are usually unwashed and may contain soluble salts of silver, it is usually desirable, and in most cases essential for the best results, that the soluble by-products of the reaction by which the silver-halides have been prepared, and any chemicals with which the silver halides may have been treated during the emulsion making operations, should be removed at some stage before the emulsion is coated upon its final support.

It is the usual practice to form the silver halides by double decomposition in a gelatin solution so that the silver halides remain suspended in the solution. In order to remove the soluble by-products of the reaction by which the silver halides have been formed, or to remove other chemicals from the gelatin solution, it is necessary to adopt one of two courses. Either the silver halide must be separated from the gelatin solution, or the silver halide-gelatin suspension must itself be washed.

As an example of the first method of procedure, the suspension of silver halide in gelatin may be centrifuged. This method presents the difficulty, however, that if the centrifuging is relatively mild, the finer particles of silver halide are not removed from the suspension and considerable loss occurs, whereas on the other hand, if the centrifuging is relatively severe, the particles pack together to form aggregates which do not readily break down when subsequently emulsified in gelatin. Moreover the method is laborious and expensive.

The second method is almost universally adopted in practice. In this method the gelatin suspension is allowed to set, for example by chilling (possibly after the addition of further gelatin), is shredded and the shredded suspension is then washed with water.

It has been observed that, in the case of solutions of proteins such as gelatin, provided the pH value of the protein solution is low or there is a salt which is an electrolyte present when the pH value need not necessarily be low, the addition of small proportions of anion soaps to the protein solutions causes the separation of a phase which contains a considerably higher concentration of the protein than the original solution, the separated protein being associated with the anion soap.

It has been further observed that where finely

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divided matter is held in suspension in the solution under treatment, such finely divided matter sediments out with the separated protein phase.

Furthermore, we have found that the addition of amounts of anion soap considerably less than those required to effect a rapid separation of a protein/anion soap complex from a protein solution free from suspended matter, are sufficient to cause, when added to a protein solution containing finely divided matter in suspension, the separation of a complex containing substantially the whole of the suspended matter.

The exact nature of the reaction between the anion soap and the protein is not clear, but it appears likely that the anion soap forms, with the protein, in the presence of a weak acid or dilute electrolyte, a loosely bound complex which separates out from the main solution.

According to the present invention, therefore, in the production of silver halide emulsions in gelatin or other protein colloid, the step of freeing the emulsion from unwanted water-soluble constituents is effected by adding to the suspension of silver halide in gelatin or other protein colloid at a low pH value or in the presence of an electrolyte (which may be the salt or salts which it is desired to remove) sufficient of an anion soap to cause precipitation of the protein phase containing the silver halide (and also the anion soap) and subjecting this phase to a washing operation.

The substances which possess the specific property of causing the separation from dilute aqueous protein solutions of a phase containing a higher concentration of protein than the original solution, and which are employed in the present invention, are classified generically as anion soaps. These 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 eight or more carbon atoms as, for example, oleic, ricinoleic, linoleic, stearic and palmitic acids.

These, however, are in general much less satisfactory 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 eight carbon atoms, as for example, the soluble salts of lauryl hydrogen sulphate and oleyl hydrogen sulphate,

(d) Soluble salts of sulphated secondary alcohols containing at least eight 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.

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 compounds 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 carbonamide group

(—NH.CO—).

Very many "anion soaps" are commercially marketed as detergents and these commercial products may conveniently be employed in the process of this invention.

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 indicated above, it appears to be essential to the success of the process that the pH value of the treated solution should be low or there is a salt which is an electrolyte present when the pH value need not necessarily be low. Generally speaking the pH should not be greater than the isoelectric point of the protein employed. Suitable electrolytes are the soluble salts of mono, di- and tri-valent acids such as ammonium nitrate, sodium chloride, magnesium sulphate and potassium citrate.

In general, the quantity of the anion soap required to effect satisfactory sedimentation of suspended matter from a protein solution depends on the protein concentration and on such other factors as the pH value of the solution, the concentration of the electrolyte present and the nature of the anion soap itself. It is not possible, therefore, to define exactly the best conditions for all sets of circumstances, but the optimum conditions for any particular case can readily be ascertained by trial.

As indicated above, the quantities of anion soap necessary to effect sedimentation of finely divided matter held in suspension in a protein solution are in general less than those required to effect the satisfactory separation of a protein phase not containing finely divided matter in suspension. The following table illustrates the difference:

Anion Soap	Amount of anion soap required to cause sedimentation of protein phase in the presence of silver halide	Amount of anion soap required to cause separation of protein phase, no suspended matter being present
	Per cent	*Per cent*
Dodecyl Sodium Sulphate	0.20	0.66
Tetradecyl Sodium Sulphate	0.15	0.66
Hexadecyl Sodium Sulphate	0.24	0.74
Lauryltriethanolamine Sulphate	0.29	0.83

The figures in the first column of the above table were obtained by the treatment of a 0.5% gelatin solution containing ammonium nitrate in a concentration of 0.5 normal and containing 1.43% silver iodo-bromide in suspension, and the figures in the second column were obtained by the treatment of a similar solution containing no silver iodo-bromide.

The separated protein phase containing the originally suspended silver halide may be washed with water and re-dispersed in a suitable liquid, or it may be directly re-dispersed in a suitable liquid, for example predominantly aqueous ethyl alcohol, or an aqueous ethyl alcoholic solution of gelatin, reprecipitated by the addition of an excess of an organic non-solvent, e. g. further ethyl alcohol and then washed. By this latter method the anion soap, or most of it, is removed from the product.

The invention thus affords a means for forming a silver halide suspension in the protein vehicle freed from unwanted salts or other substances which may have been present in the original suspension.

The usual procedure in making photographic emulsions is to form the emulsion, ripen it, wash it and then digest and add any special additions required, e. g. sensitising dyes. It is preferred that this order of operations be carried out in the present case, the washing operation being carried out by the method of this invention.

The invention is illustrated by the following examples:

Example I

Various anion soaps were added to 100 ccs. of a solution containing 1.43% of silver iodo-bromide in suspension and 0.5% gelatin, and containing ammonium nitrate in a concentration of 0.5 normal, the pH value of the solution being about 6.0. The soap additions were made at 125° F. and substantially complete sedimentation of the suspended silver ido-bromide was effected in five minutes by the addition of each of the following solutions:

(a) 5 ccs. of a 10% solution of lauryl triethanolamine sulphate.

(b) 7.5 ccs. of a 10% solution of the sodium salt of alkyl naphthalene sulphonic acid.

(c) 5 ccs. of a 10% solution of the sodium salt of alkyloxy-diphenyl disulphonic acid.

The same quantities of anion soap were effective in causing the substantially complete sedimentation of the silver iodo-bromide when ammonia was added to the solution to bring the pH value to 9.5.

The sedimented complexes containing the originally suspended silver iodo-bromide may be re-dispersed in warm water or, more easily, in warm aqueous alcohol (e. g. 40% alcohol) or in a warm gelatin solution.

Example II

Various anion soaps were added to 100 ccs. of a solution containing 1.43% silver iodo-bromide in suspension and 0.5% gelatin, the solution being made acid with N/100 sulphuric acid so that its pH value was 2.2. The substantially complete sedimentation of the suspended silver iodo-bromide was effected in five minutes by the addition of each of the following solutions:

(a) 3 ccs. of a 10% solution of lauryl triethanolamine sulphate.

(b) 4 ccs. of a 10% solution of the sodium salt of alkyl naphthalene sulphonic acid.

(c) 5 ccs. of a 10% solution of the sodium salt of alkyloxy-diphenyl disulphonic acid.

The sedimented complexes containing the originally suspended silver iodo-bromide may be re-dispersed by warming them with weak alkali solution (e. g. 1% borax solution) or by warming them with a gelatin solution.

Example III

To 1 litre of an aqueous photographic emulsion at 125° F. containing suspended silver halides 11.5%, ammonium nitrate 0.6 N, ammonium bromide 0.06 N, ammonia 0.5 N, and gelatin 0.4%, is added 8 ccs. of a 20% aqueous solution of a mixture of secondary alkyl sodium sulphates, mainly dodecyl and tetradecyl, stirring thoroughly for 30 seconds. After 10 minutes the clear supernatant liquid is decanted and the residue dispersed in the following solution at 125° F.:

Gelatin	gms	16
Water	ccs	110
Ethyl alcohol	ccs	25

To the completely dispersed liquid an addition of 500 ccs. of ethyl alcohol (64° O. P.) is made, which results in the precipitation of the gelatin, bearing the silver halides. The supernatant aqueous spirit containing the wetting agent is easily decanted from the precipitate, which is then soaked in water, and re-dispersed in gelatin in known manner to form a photographic emulsion substantially free from the salts present in the original emulsion.

It is to be noted that the quantities of anion soap given in the above examples are not the minimum concentrations which will cause sedimentation, but are such concentrations as will cause rapid sedimentation of the suspended matter to take place. Where the anion soap employed is very active in causing the sedimentation of suspended matter, it is frequently preferable to add the anion soap solution in successive portions allowing the suspension to settle between such additions, as a more complete sedimentation may be effected in this way.

The precipitated silver halide-gelatin formed by the process of this invention may be used to form a highly concentrated emulsion suitable for drying to form solid dry particulate emulsions which may be marketed as such for dispersion to form normal aqueous emulsions when required. The term "dry" in this connection means that the emulsion does not contain any substantial excess of water over that which the gelatin naturally holds in equilibrium with the atmosphere.

Although the above examples are concerned with the treatment of gelatin solutions, it is to be noted that solutions of other proteins containing finely divided light-sensitive matter in suspension may also be treated by the process of this invention, e. g. suspensions of silver halides in albumin or casein.

What we claim is:

1. Process for the production of an organic complex containing silver halide in suspension which comprises forming a suspension of silver halide in an aqueous solution of gelatin, and adding to such suspension, in the presence of an electrolyte, sufficient of an anion soap to cause precipitation of the gelatin phase containing the silver halide and separating the so-formed gelatin/anion soap complex containing silver halide.

2. Process for the production of an organic complex containing silver halide in suspension which comprises forming a suspension of silver halide by precipitating such salt in an aqueous solution of gelatin, and adding to such suspension, in the presence of an acid so that the emulsion has a low pH value, sufficient of an anion soap to cause precipitation of the gelatin phase containing the silver halide and separating the so-formed gelatin/anion soap complex containing silver halide.

3. Process for the production of an organic complex containing silver halide in suspension which comprises forming a suspension of silver halide by precipitating such salt in an aqueous solution of gelatin, and adding to such suspension, at a pH value not substantially greater than the isoelectric point of the gelatin, sufficient of an anion soap to cause precipitation of the gelatin phase containing the silver halide and separating the so-formed gelatin/anion soap complex containing silver halide.

4. Process for the production of an organic complex containing silver halide in suspension which comprises forming a suspension of silver halide by precipitating such salt in an aqueous solution of gelatin, and adding to such suspension, in the presence of an electrolyte, sufficient of a soluble salt of an alkyl sulfonic acid of at least eight carbon atoms to cause precipitation of the gelatin phase containing the silver halide and separating the so-formed gelatin/anion soap complex containing silver halide.

5. Process for the production of an organic complex containing silver halide in suspension which comprises forming a suspension of silver halide in an aqueous solution of gelatin, and adding to such emulsion, in the presence of an electrolyte, sufficient of a soluble salt of a sulphated fatty alcohol of at least eight carbon atoms to cause precipitation of the gelatin phase containing the silver halide and separating the so-formed gelatin/anion soap complex containing silver halide.

6. Process for the production of an organic complex containing silver halide in suspension which comprises forming a suspension of silver halide in an aqueous solution of gelatin, and adding to such emulsion, in the presence of an electrolyte, sufficient of a soluble salt of an alkylated aromatic sulfonic acid to cause precipitation of the gelatin phase containing the silver halide and separating the so-formed gelatin/anion soap complex containing silver halide.

7. Process for the production of silver halide emulsions in gelatin which comprises forming an aqueous emulsion of precipitated silver halide in gelatin, adding to such emulsion, in the presence of an electrolyte, sufficient of an anion soap to cause precipitation of the gelatin phase containing the silver halide, subjecting this phase to a washing operation, and thereafter re-dispersing this phase in an aqueous medium.

8. Process for the production of silver halide emulsions in gelatin which comprises forming an aqueous emulsion of precipitated silver halide in gelatin, adding to such emulsion, in the presence of an acid so that the emulsion has a low pH value, sufficient of an anion soap to cause precipitation of the gelatin phase containing the silver halide, subjecting this phase to a washing operation, and thereafter re-dispersing this phase in an aqueous medium.

9. Process for the production of silver halide emulsions in gelatin which comprises forming an aqueous emulsion of precipitated silver halide in gelatin, adding to such emulsion, at a pH value

not substantially greater than the isoelectric point of the gelatin, sufficient of an anion soap to cause precipitation of the gelatin phase containing the silver halide, subjecting this phase to a washing operation, and thereafter re-dispersing this phase in an aqueous medium.

10. Process for the production of silver halide emulsions in gelatin which comprises forming an aqueous emulsion of precipitated silver halide in gelatin, adding to such emulsion, in the presence of an electrolyte, sufficient of a soluble salt of an alkyl sulfonic acid of at least eight carbon atoms to cause precipitation of the gelatin phase containing the silver halide, subjecting this phase to a washing operation, and thereafter re-dispersing this phase in an aqueous medium.

11. Process for the production of silver halide emulsions in gelatin which comprises forming an aqueous emulsion of silver halide in gelatin, adding to such emulsion, in the presence of an electrolyte, sufficient of a soluble salt of a sulphated fatty alcohol of at least eight carbon atoms to cause precipitation of the gelatin phase containing the silver halide, subjecting this phase to a washing operation, and thereafter re-dispersing this phase in an aqueous medium.

12. Process for the production of silver halide emulsions in gelatin which comprises forming an aqueous emulsion of silver halide in gelatin, adding to such emulsion, in the presence of an electrolyte, sufficient of a soluble salt of an alkylated aromatic sulfonic acid to cause precipitation of the gelatin phase containing the silver halide, subjecting this phase to a washing operation, and thereafter re-dispersing this phase in an aqueous medium.

13. Process for the production of a silver halide emulsion in gelatin which comprises forming an aqueous emulsion of precipitated silver halide in gelatin, ripening it, adding to it, in the presence of an electrolyte, sufficient of an anion soap to cause precipitation of the gelatin phase containing the silver halide, subjecting this phase to a washing operation, and thereafter re-dispersing this phase in an aqueous medium, and digesting it.

14. Process for the production of a silver halide emulsion in gelatin which comprises forming an aqueous emulsion of precipitated silver halide in gelatin, ripening it, adding to it, in the presence of an acid so that the emulsion has a low pH value, sufficient of an anion soap to cause precipitation of the gelatin phase containing the silver halide, subjecting this phase to a washing operation, and thereafter re-dispersing this phase in an aqueous medium, and digesting it.

15. Process for the production of silver halide emulsions in gelatin which comprises forming an aqueous emulsion of precipitated silver halide in gelatin, adding to such emulsion, in the presence of an electrolyte, sufficient of an anion soap

to cause precipitation of the gelatin phase containing the silver halide, subjecting this phase to a washing operation, and thereafter re-dispersing this phase in an aqueous medium, and thereafter drying the emulsion down to form a dry particulate emulsion.

16. Process for the production of silver halide emulsions in gelatin which comprises forming an aqueous emulsion of precipitated silver halide in gelatin, adding to such emulsion, in the presence of an electrolyte, sufficient of an anion soap to cause precipitation of the gelatin phase containing the silver halide, subjecting this phase to a washing operation, and thereafter re-dispersing this phase in a liquid medium.

17. Process for the production of silver halide emulsions in gelatin which comprises forming an aqueous emulsion of precipitated silver halide in gelatin, adding to such emulsion, in the presence of an electrolyte, sufficient of an anion soap to cause precipitation of the gelatin phase containing the silver halide, subjecting this phase to a washing operation, and thereafter re-dispersing this phase in a liquid medium containing ethyl alcohol.

18. Process for the production of silver halide emulsions in gelatin which comprises forming an aqueous emulsion of precipitated silver halide in gelatin, adding to such emulsion, in the presence of an acid so that the emulsion has a low pH value, sufficient of an anion soap to cause precipitation of the gelatin phase containing the silver halide, subjecting this phase to a washing operation, and thereafter re-dispersing this phase in a liquid medium.

19. Process for the production of silver halide emulsions in gelatin which comprises forming an aqueous emulsion of precipitated silver halide in gelatin, adding to such emulsion, in the presence of an acid so that the emulsion has a low pH value, sufficient of an anion soap to cause precipitation of the gelatin phase containing the silver halide, subjecting this phase to a washing operation, and thereafter re-dispersing this phase in a liquid medium containing ethyl alcohol.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,290,794	Sheppard	Jan. 7, 1919
1,844,716	Lambert	Feb. 9, 1932

OTHER REFERENCES

Journal of the American Chemical Society, Dec. 1943, pages 2187–2190, and May 1944, pages 692–697.