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PREPARATION OF PHOTOGRAPHIC EMULSIONS

Jean E. Jones and Albert E. Ballard, Rochester, N. Y., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

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This invention relates to methods of preparing photographic silver halide emulsions and more particularly to a process of forming photographic emulsions wherein by-products are removed; for example, by means of vacuum.

In the Damschroder U. S. patent application, Serial No. 68,743, field concurrently herewith, now U. S. Patent 2,646,426, is described and claimed a process of making photographic emulsions according to which an aqueous ammoniacal solution of a silver compound, such as silver oxide and silver carbonate, is reacted with an amine halide including ammonium halides and lower aliphatic amine halides such as methyl ammonium halides. The result is to obtain a reaction mixture containing silver halide and substantially no other non-volatile reaction products and from which the volatile products are completely removable by means of vaporization as well as washing. The resulting silver halide emulsions are suitable for use in making light-sensitive photographic emulsions adaptable to any of the well-known uses for the so-called washed type of emulsion.

In the above process, it is apparent that when utilizing ammoniacal silver oxide solutions, it is of utmost importance that precautions be taken in dissolving silver oxide in ammoniacal solution and the manner in which such solutions are handled because of the highly explosive nature of the system. One method of lessening the danger which is not too reliable includes keeping the silver oxide moist at all times. Such precautions may still fail if the ammoniacal silver oxide solutions are allowed to form dried residues on the walls of containers. Another method disclosed in the mentioned Damschroder invention includes incorporating a colloid such as gelatin in the ammonia solution before dissolving the silver compound.

Another somewhat troublesome characteristic of the basic process of making emulsions as described in the Damschroder invention lies in the fact that equipment, particularly metal apparatus used in the manufacture of the emulsions, becomes coated with silver which impairs operation especially of moving parts and reduces the efficiency of the process.

We have discovered quite unexpectedly that when ammonium salts of organic and inorganic oxygen-containing acids such as ammonium nitrate, carbonate, sulfate, citrate, acetate or oxalate are incorporated into the reaction mixture, not only is the silver plating tendency of the system reduced but also the explosive characteristic of the system, particularly of dried residues thereof, is destroyed. Also when ammonium carbonate is utilized as the inhibitor, we are able to employ appreciably less ammonia in the conversion of silver oxide to the ammono compound. Also when utilizing ammonium carbonate the ammoniacal silver oxide solution may be used for forming emulsions from which all reaction products may be separated from the silver halide by vaporization as well as by washing.

One object of our invention therefore is to provide non-explosive ammoniacal silver oxide systems of particular use in forming silver halide emulsions. Another object is to provide agents which inhibit the detonating and plating tendencies of ammoniacal silver oxide systems. A further object is to provide methods of making photographic emulsions utilizing the inhibitors of the invention. Other objects include using vaporization methods for the purification of such emulsions as will be apparent from the following description of our invention.

The objects of our invention are accomplished in part by incorporating ammonium salts into ammoniacal silver oxide solutions, preferably before conversion of the silver oxide to the ammono compound. Apparently the inhibiting effect of the ammonium salts is due to a buffering effect. That is, it appears necessary, in order to prevent violent decomposition of the dried ammoniated silver oxide system, to decrease the pH below that of the unstable system, and this is accomplished according to our invention by the addition of water-soluble ammonium salts of oxygen-containing acids such as ammonium nitrate, ammonium sulfate, ammonium carbonate, etc. A pH of 13.2 measured at 25° C. with glass electrodes, was obtained for a highly explosive composition resulting from the conversion of the silver oxide from 0.1 equivalent of silver nitrate with a 10% excess of concentrated aqueous ammonia solution and dilution with water to 175 cc. A similar composition, which was non-explosive, made by combining 0.1 equivalent of moist silver oxide with a solution of 0.062 equivalent of ammonium carbonate, then converting the silver salt with 10% excess ammonia and diluting to 175 cc. had a pH of 12.9. Ammoniated silver carbonate systems are not explosive and a pH value of 12.0 was recorded for the system obtained, when 0.1 equivalent of silver carbonate was converted with 10% excess ammonia and diluted to 175 cc.

The ammonium salt inhibitors are effective in a fairly wide range of concentration giving satisfactory protection in the majority of cases within a range of from about 0.5 to 1.0 equivalent of ammonium salt per equivalent of silver nitrate which had been converted to silver oxide although more salt can be used as shown in the table following, the starred values of which indicate preferred amounts. The various ammonium salts vary somewhat in their efficiency as inhibitors as may be seen from the following table illustrating results obtained with typical ammonium salts.

Ammonium salt	Equivalents of salt per equivalent $AgNO_3$	cc. conc. ammonia solution per mol $AgNO_3$ for conversion	Degree of protection afforded (percent)	No. of Trials
Ammonium Carbonate	.5	229	0	12
Do	*.552	200	97.4	114
Do	.6	186	100	506
Do	.742	143	100	12
Ammonium Nitrate	.25	283	0	12
Do	.425	255	25	12
Do	*.53	226	100	36
Do	1.06	141	100	38
Ammonium Sulfate	.308	283	0	12
Do	.516	226	42	12
Do	*.644	226	100	42
Do	1.29	198	100	40
Ammonium Acetate	0.4	226	0	39
Do	*0.5	226	92	35
Do	0.625	226	100	36
Ammonium Citrate	0.399	226	6	35
Do	*0.495	226	100	36
Do	0.585	226	100	36
Ammonium Oxalate	*0.56	226	95	36
Do	0.68	226	100	36

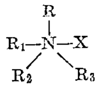
The above data were obtained by converting samples of 1.2 parts of silver nitrate in ten parts of water to silver oxide by treatment with 0.31 part of sodium hydroxide in five parts of water followed by washing and centrifuging the precipitates. Thereafter, varying amounts of 20 per cent solutions of the ammonium salts were added to the individual samples followed by the amount of concentrated ammonium hydroxide required to dissolve the precipitated silver oxide and diluting to 10 cc. The protection against detonation afforded by the treatments was ascertained by evaporation of portions of the samples to dryness and attempting to explode the dried residues. The degree of protection was calculated from the number of detonations obtained and the number of trials made. In a similar manner, a number of samples of silver oxide treated with 0.3 mol (0.6 equivalent) of ammonium carbonate per mol of silver nitrate converted to silver oxide were aged from 1-14 days and since the dried samples which had been aged failed to detonate after this time, it appeared that the ammonium salt could be considered to give reasonably permanent protection against the explosive tendencies of the system.

The following example is provided as illustrative of methods we employ for making photographic emulsions from ammoniacal silver oxide solutions protected by the ammonium salts of the invention.

Example

Silver oxide is prepared in the usual manner by treating an aqueous solution of silver nitrate with an excess of aqueous sodium hydroxide solution. The precipitate is then washed several times and to 0.125 mol of moist silver oxide is added a solution of 0.073 mol of ammonium carbonate monohydrate in 170 cc. of water. The mixture is then treated with 88 cc. of 28 per cent aqueous ammonia solution and then diluted to 380 cc. The solution of the complex silver compound obtained is added to a solution of 0.264 mol of ammonium bromide, 0.0053 mol of potassium or ammonium iodide and 6.1 grams of gelatin in a total volume of 380 cc. After the precipitation of the silver halide is complete, the excess ammonia and substantially all of the ammonium carbonate are removed by vaporization; that is, passing the mixture through a vacuum apparatus of the type and in the manner described in the Damschroder invention mentioned. The resulting emulsion is then treated by methods well known in the art including digestion steps and after addition of suitable materials such as sensitizing agents and additional gelatin, is coated on film base. Sensitometric tests on exposed samples of the film showed the emulsion possessed speed and contrast characteristics comparable to fine-grained negative emulsions. During the preparation of the above emulsion, it was found that dried residues of the silver compound could not be detonated. In a similar manner, we incorporate various amounts of the ammonium salts into the ammoniated silver solution in the proportions indicated in the above table and react these solutions in the presence of gelatin or other peptizing lyophilic colloid of the type disclosed in the Damschroder invention, with one or more water-soluble halides such as ammonium halide.

It will be apparent from the above description that one embodiment of our invention includes making photographic emulsions by reacting an aqueous ammonia solution of silver oxide in the presence of a lyophilic colloid such as gelatin and an ammonium salt of an oxygen-containing acid such as ammonium carbonate, with one or more alkali metal or alkaline earth metal halides such as sodium bromide or calcium bromide, with hydrogen halides such as hydrobromic or hydrochloric acids and amine halides such as pyridinium hydrobromide, ammonium bromide, chloride or iodide and other halides having the structure



$$R_1-\overset{\displaystyle R}{\overset{|}{N}}-X \quad (R_2,\ R_3 \text{ on } N)$$

where X is a halogen atom and R, R_1, R_2, and R_3 each represent a member selected from the group consisting of a hydrogen atom and an alkyl group having from 1-4 carbon atoms, the sum total of the carbon atoms in the R groups being from 0-4, then removing volatile product from the resulting reaction mixture by means of washing or a vaporization method such as by means of vacuum. While a number of other ammonium salts of both organic and inorganic acids are effective in our process, we prefer to use ammonium carbonate, ammonium acetate and ammonium sulfate as the protective agents against the detonating and plating effects mentioned. Of the three ammonium salts mentioned, we prefer ammonium carbonate because it is readily removable from emulsions by vacuum treatment as well as by washing in the conventional manner. Ammonium acetate and ammonium sulfate are effective, as has been shown previously, but their use is limited to cases where it is not necessary to produce completely salt-free emulsions by vaporization methods, but of course they may be utilized if washing is employed for purification of the emulsion. However, in these cases we may use evacuation for removal of excess ammonia, if desired, and the salt content of the emulsion can be kept to a minimum by use of the least amount of the salt which will furnish the desired protection against detonation.

Here and in the appended claims where reference is made to vaporization, it is to be understood that this includes subjecting a system containing dissolved volatile matter to methods of removing the same in the presence of nonvolatile product and water, such as by vacuum, passing air over the reaction mixture, raising the temperature of the system to increase the rate of removal of dissolved product or a combination of any of these methods. Similarly, by the term "ammoniacal" as used in reference to silver oxide solutions, we mean solutions in which silver oxide is converted to the ammono compound by means of ammonia or a lower aliphatic amine, and "ammoniated" as applied to silver oxide denotes silver oxide reacted with ammonia or amines to the extent that the silver compound is in the form useful for making silver halide emulsions and dried residues thereof can be detonated.

It is to be understood that the disclosure herein is by way of example and that we consider as included in our invention all modifications and equivalents falling within the scope of the appended claims.

What we claim is:

1. The method of making a photographic silver halide emulsion which comprises preparing an ammoniacal solution of silver oxide by dissolving moist silver oxide in an aqueous ammonia solution, adding to the ammoniacal solution from about 0.5 to 1.0 molecular equivalent, based on the silver salt used in making the oxide, of ammonium acetate, forming silver halide by reaction of the resulting solution in the presence of a silver halide peptizing hydrophilic colloid with a water-soluble halide, and removing volatile product from the resulting reaction mixture.

2. The method of making a photographic silver halide emulsion which comprises preparing an ammoniacal solution of silver oxide by dissolving moist silver oxide in an aqueous ammonia solution, adding to the ammoniacal solution from about 0.5 to 1.0 molecular equivalent, based on the silver salt used in making the oxide, of ammonium acetate, forming silver halide by reaction of the resulting solution in the presence of a silver halide peptizing hydrophilic colloid with a water-soluble halide, and removing volatile product from the resulting reaction mixture by vaporization.

3. The method of making a photographic silver halide emulsion which comprises preparing an ammoniacal solution of silver oxide by dissolving moist silver oxide in an aqueous ammonia solution, adding to the ammoniacal solution from about 0.5 to 1.0 molecular equivalent, based on the silver salt used in making the oxide, of ammonium acetate, forming silver halide by reaction of the resulting solution in the presence of a silver halide peptizing hydrophilic colloid with a water-soluble halide, and removing volatile product from the resulting reaction mixture by vacuum.

4. The method of making a photographic silver halide emulsion which comprises preparing an ammoniacal solution of silver oxide by dissolving moist silver oxide in an aqueous ammonia solution, adding to the ammoniacal solution from about 0.5 to 1.0 molecular equivalent, based on the silver salt used in making the oxide, of ammonium sulfate, forming silver halide by reaction of the resulting solution in the presence of a silver halide peptizing hydrophilic colloid with a water-soluble halide, and removing volatile product from the resulting reaction mixture.

5. The method of making a photographic silver halide emulsion which comprises preparing an ammoniacal solution of silver oxide by dissolving moist silver oxide in an aqueous ammonia solution, adding to the ammoniacal solution from about 0.5 to 1.0 molecular equivalent, based on the silver salt used in making the oxide, of ammonium sulfate, forming silver halide by reaction of the resulting solution in the presence of a silver halide peptizing hydrophilic colloid with a water-soluble halide, and removing volatile product from the resulting reaction mixture by vaporization.

6. The method of making a photographic silver halide emulsion which comprises preparing an ammoniacal solution of silver oxide by dissolving moist silver oxide in an aqueous ammonia solution, adding to the ammoniacal solution from about 0.5 to 1.0 molecular equivalent, based on the silver salt used in making the oxide, of ammonium sulfate, forming silver halide by reaction of the resulting solution in the presence of a silver halide peptizing hydrophilic colloid with a water-soluble halide, and removing volatile product from the resulting reaction mixture by vacuum.

7. The method of making a photographic silver halide emulsion which comprises preparing an ammoniacal solution of silver oxide by dissolving moist silver oxide in an aqueous ammonia solution, adding to the ammoniacal solution from about 0.5 to 1.0 molecular equivalent, based on the silver salt used in making the oxide, of ammonium carbonate, forming silver halide by reaction of the resulting solution in the presence of a silver halide peptizing hydrophilic colloid with a water-soluble halide and removing volatile product from the resulting reaction mixture.

8. The method of making a photographic silver halide emulsion which comprises preparing an ammoniacal solution of silver oxide by dissolving moist silver oxide in an aqueous ammonia solution, adding to the ammoniacal solution from about 0.5 to 1.0 molecular equivalent, based on the silver salt used in making the oxide, of ammonium carbonate, forming silver halide by reaction of the resulting solution in the presence of a silver halide peptizing hydrophilic colloid with a water-soluble halide and removing volatile product from the resulting reaction mixture by vaporization.

9. The method of making a photographic silver halide emulsion which comprises preparing an ammoniacal solution of silver oxide by dissolving moist silver oxide in an aqueous ammonia solution, adding to the ammoniacal solution from about 0.5 to 1.0 molecular equivalent, based on the silver salt used in making the oxide, of ammonium carbonate, forming silver halide by reaction of the resulting solution in the presence of a silver halide peptizing hydrophilic colloid with a water-soluble halide and removing volatile product from the resulting reaction mixture by vacuum.

10. The method of making a photographic silver halide emulsion which comprises preparing an ammoniacal solution of silver oxide by dissolving moist silver oxide in an aqueous ammonia solution, adding to the ammoniacal solution from about 0.5 to 1.0 molecular equivalent, based on the silver salt used in making the oxide, of an

ammonium salt selected from the group consisting of ammonium carbonate, ammonium nitrate, ammonium sulfate, ammonium acetate, ammonium citrate, and ammonium oxalate, forming silver halide by reaction of the resulting solution in the presence of a silver halide peptizing hydrophilic colloid with a water-soluble halide, and removing volatile product from the resulting reaction mixture.

11. The method of making a photographic silver halide emulsion which comprises preparing an ammoniacal solution of silver oxide by dissolving moist silver oxide in an aqueous ammonia solution, adding to the ammoniacal solution from about 0.5 to 1.0 molecular equivalent, based on the silver salt used in making the oxide, of an ammonium salt selected from the group consisting of ammonium carbonate, ammonium nitrate, ammonium sulfate, ammonium acetate, ammonium citrate, and ammonium oxalate, forming silver halide by reaction of the resulting solution in the presence of a silver halide peptizing hydrophilic colloid with a water-soluble halide, and removing volatile product from the resulting reaction mixture by means of vaporization.

12. The method of making a photographic silver halide emulsion which comprises preparing an ammoniacal solution of silver oxide by dissolving moist silver oxide in an aqueous ammonia solution, adding to the ammoniacal solution from about 0.5 to 1.0 molecular equivalent, based on the silver salt used in making the oxide, of an ammonium salt selected from the group consisting of ammonium carbonate, ammonium nitrate, ammonium sulfate, ammonium acetate, ammonium citrate, and ammonium oxalate, forming silver halide by reaction of the resulting solution in the presence of a silver halide peptizing hydrophilic colloid with a water-soluble halide, and removing volatile product from the resulting reaction mixture by means of vacuum evacuation.

13. The method of preparing a photographic silver halide emulsion which comprises preparing an ammoniacal solution of silver oxide by dissolving moist silver oxide in an aqueous ammonia solution, adding to the ammoniacal solution from about 0.5 to 1.0 molecular equivalent, based on the silver salt used in making the oxide, of ammonium nitrate, forming silver halide by reaction of the resulting solution in the presence of a silver halide peptizing hydrophilic colloid with a water-soluble halide, and removing volatile product from the reaction mixture.

14. The method of preparing a photographic silver halide emulsion which comprises preparing an ammoniacal solution of silver oxide by dissolving moist silver oxide in an aqueous ammonia solution, adding to the ammoniacal solution from about 0.5 to 1.0 molecular equivalent, based on the silver salt used in making the oxide, of ammonium citrate, forming silver halide by reaction of the resulting solution in the presence of a silver halide peptizing hydrophilic colloid with a water-soluble halide, and removing volatile product from the reaction mixture.

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