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PREPARATION OF PHOTOGRAPHIC SILVER HALIDE EMULSIONS UTILIZING POLYOXYALKYLENATED GELATING DERIVATIVES

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ABSTRACT OF THE DISCLOSURE

A method for preparing silver halide dispersions by mixing aqueous solutions of silver nitrate and alkali metal halides in the presence of a polyoxyalkylenated derivative of gelatin to form a silver halide-polyoxyalkylenated gelatin dispersion, followed by coagulation and recovery of the dispersion.

This invention relates, in general, to photography and in particular to the preparation of silver halide dispersions in a water-permeable material having protective colloid properties.

The conventional methods heretofore employed commercially for the preparation of silver halide dispersions in a protective colloid carrier such as gelatin involve, as essential sequential operations, the reaction of a water-soluble silver salt such as silver nitrate, with at least one water-soluble halide such as potassium or sodium bromine, preferably together with potassium or sodium iodide, in an aqueous solution of a gelatin colloid peptizing agent. The dispersion of silver halide thus formed contains water-soluble salts as a by-product of the double decomposition reaction, in addition to an unreacted excess of either of the initial salts. In such methods wherein gelatin is employed as the peptizer, the methods have been, in the past, limited in scope by the physical properties peculiarly characteristic of gelatin. These physical properties have necessitated the use of concentrations of silver halide and a gelatin sometimes, which are not the most desirable for photographic products. For instance, emulsions of high concentrations of silver halide have proved difficult to prepare. Limitations have also been imposed upon the method regarding the conditions of dilutions during the emulsion preparation since emulsions of very high water content are difficult to coat and dry. Often, the technician has been obliged to limit the minimum concentration of gelatin in the washing operation in which soluble salts are removed.

It has been considered desirable, in the case of photographic emulsions, particularly those to be coated on water-impermeable supports, such as film base, that the soluble salts present in the emulsion be reduced in concentration. It has been the practice previously, where gelatin has been used as the protective colloid, to remove the soluble materials therefrom by setting the gel dispersion by means of chilling and noodling the so-set dispersion and washing the noodles in cold water. Under such conditions, a minimum gelating concentration of approximately 3–4% is required under practical conditions, and this limitation has hampered the operations of the emulsion maker in his preparation of emulsions by this method. Moreover, this method has the distinct disadvantage in that the solidification, noodle formation and washing operations are time-consuming. Furthermore, such operations must be accomplished in the presence of an amount of binding agent which cannot be reduced to the extent desired. 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 silver salt should be present per unit of surface coating. In an attempt to remedy the foregoing situation, emulsion concentration has been effected by driving off the water present, as, for example, by evaporation. However, according to this method, the proportion of binding agent to light-sensitive salt remains unchanged. Consequently, a more concentrated emulsion is only obtained at the expense of a high viscosity, which can hinder the coating of the emulsion to the extent of necessitating the use of special coating methods.

In an effort to overcome or otherwise mitigate the shortcomings inherent in the procedures described above, more recent methods are based on silver halide precipitation techniques for the purpose of rendering noodle formation as well as extended washing operations unnecessary. In such method, the emulsions are coagulated by adding a precipitant to remove the excess salts, with the coagulate being separated from the supernatant aqueous solution containing the salts in dissolved form, washed with water and, after adding more gelatin solution, often also re-dispersed by adjusting the pH to a predetermined value. It is possible in this way to obviate the rinsing operation thus effecting a considerable saving in time. In addition, the emulsion character can be varied greatly and improvements in the photographic properties can be obtained. The increasing importance of this flocculation process is illustrated by the large selection of variants of the process which have become known in recent times. However, the flocculation of precipitation methods thus far proposed have been found to suffer from one or more disadvantages which greatly reduce their over-all effectiveness. For example, the methods currently enjoying relatively widespread use require relatively large quantities of precipitating agent in order to achieve silver halide-gelatin dispersions of the requisite photographic qualities. The latter consideration assumes considerable importance when it is realized that many of the extensively used precipitating agents are relatively expensive and in many cases inflammable thereby presenting a variety of problems with respect to storage, handling and the like.

In addition, such methods present considerable difficulty in connection with the digestion and washing operations. The latter operation usually requires copious amounts of water while the former operation has characteristically resulted in the introduction of undesirable physical properties into the emulsion batch. As a consequence, this situation has necessitated the application of certain remedial measures such as corrective changes in the emulsion formulation. This, in turn, may oftentimes be at the expense of properties considered desirable if not essential in the final product. Moreover, the physical ripening of gelatin hydrolysates is not entirely satisfactory for the further reason that such hydrolysates may possess insufficient carrying power and undesired sedimentation of the silver halide may thus occur. This, combined with the large amounts of water required in the washing operation make difficult the obtention of silver halide emulsions with the desired silver halide content.

In accordance with the present invention, there is provided a method for preparing silver halide dispersions which greatly reduces the amount of precipitating agent required for forming the silver halide dispersion and which allows the production of photographic emulsions therewith of significantly increased silver content. Accordingly, it is an object of the present invention to provide an improved process for the preparation of silver halide dispersions in a protective colloid binder as well as the novel products produced thereby which will not be subject to one or more of the above disadvantages.

It is a further object of the present invention to provide an improved process for the preparation of dispersions of silver halide useful in the production of photographic, gelatino-silver halide emulsions characterized by outstanding improvement in silver halide colloid ratios, and wherein the amount of precipitating agent required in forming the silver halide dispersion is greatly reduced.

Other objects and advantages will appear as the description proceeds.

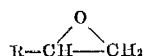
The attainment of the foregoing objects is made possible by the present invention which comprises a method of preparing a dispersion of a silver halide involving the steps of mixing together a water-soluble silver salt and at least one water-soluble halide salt in the presence of a gelatin derivative which is the reaction product of gelatin with an alkylene oxide in varying amounts to form thereby a dispersion of silver halide and polyoxyalkylenated gelatin, and coagulating and recovering the dispersion thus formed. It is highly important to the results of the present invention that the coagulation, i.e., ripening and precipitating, of the silver halide grains be effected in the presence of the gelatin-alkylene oxide adduct, this procedure forming the salient feature of the invention both described and claimed herein.

The term "gelatin" as utilized herein is intended to signify the art-accepted designation of the photographic colloid binder derived from collagen and comprising a proteinaceous substance. It is also intended to include any other product substantially identical therewith, as for example, where such product is produced synthetically. While the exact structure of the gelatin is not known, it occurs in bones, hides, skins and sinews and can be readily obtained from the parent substance, collagen, according to well known prior art treatments which usually involve some form of treatment such as degreasing in the case of bone stock and liming or acidulation in the case of hide or sinew stock, to prepare the raw material for the cooking step. The above treated raw material is hydrolyzed into gelatin by heating in water to yield thereby a solution which is concentrated by vacuum evaporation and subsequently spray or drum dried to produce a gelatin product recoverable in the form of sheets, flakes, powder, pearls or "woodles" depending upon the mode of processing.

Any form of gelatin appears to be operable for the formation of the water soluble oxide adducts thereof which are employed in the novel silver halide dispersions of the present invention.

The term "polyoxyalkylenated gelatin" is intended to include within its scope those oxide adducts obtained by reacting gelatin with an alkylene oxide, the latter being employed preferably in amounts ranging from 0.8 to 5 parts per part of gelatin. These oxide adducts may easily and conveniently be prepared by simply heating the gelatin with the particular alkylene oxide at a temperature ranging from 50° C. to 200° C. in the presence of a suitable catalyst. As examples of catalyst materials found to be suitable for the preparation of the above described gelatin-alkylene oxide adducts, there may be mentioned the alkoxides, oxides and hydroxides of lithium, potassium, sodium, calcium, zinc and lead. However, the alkali metal hydroxides such as sodium and potassium hydroxide are found to be especially suitable. Contacting of the alkylene oxide and gelatin may be effected in simple fashion by merely passing a stream of the alkylene oxide through an aqueous solution of the gelatin at temperatures within the range above stated.

The alkylene oxides which find immediate and practical application in producing the water soluble, polyoxyalkylenated gelatin derivatives contemplated for use in the present invention are preferably vicinal epoxides of the following formula:



wherein R can be hydrogen, alkyl, cycloalkyl, alkaryl, aralkyl, and the like. As examples of alkylene oxides coming within the scope of the above formula and found to be highly suitable to the purposes of the present invention, there may be mentioned ethylene oxide, propylene oxide, butylene oxide, styrene oxide, cyclohexene oxide and the like, including mixtures of two or more of the foregoing.

The term "emulsification" as used herein is intended to include those steps customarily employed in effecting silver halide-gelatin dispersion formation including the manipulative steps directed towards controlling the grain size, grain size distribution and grain sensitivity of the silver halide crystals thus formed.

Accordingly, the term "emulsification" is to be understood as comprehending "digestion" of the silver halide dispersion, the latter term having its well known art accepted significance and conoting the usual steps of heating the silver halide polyoxyalkylenated gelatin dispersion under controlled conditions of time and temperature. It is to be further understood that the ripening or digestion step may be carried out in the presence of additional ingredients such as ripening agents, stabilizers, and the like. The precipitate or flocculation of the polyoxyalkylenated gelatin-silver halide dispersion can be achieved with the use of conventional and well known agents. As examples of flocculating agents contemplated for use herein there may be mentioned long chain alkyl sulfonic acids such as those wherein the alkyl group contains from 12 to 20 carbon atoms, organic polymeric materials such as polymers and copolymers of styrene sulfonic acid and the like. In the broad sense, flocculation or precipitation as used herein is intended to include most any procedure which results in a lowering of the pH of the polyoxyalkylenated gelatin dispersion so long as the properties desired in the final emulsion product are not deleteriously affected thereby. For example, good results can be obtained when pH adjustment is effected by the use of such compounds as acid ammonium sulfate and the like.

In accordance with the present invention it is found that dispersions of silver halide, wherein the precipitation of the silver halide material is effected in the presence of a gelatin alkylene oxide adduct of the type described above, are highly suitable for use in the preparation of photographic, gelatino-silver halide emulsions of significantly increased silver contents with exceptional silver halide/gelatin ratios being obtained therewith. Moreover, with respect to the actual silver halide precipitating step, it is found that the presence of the above described polyoxyalkylenated gelatin derivatives greatly reduces the amount of the precipitating agent which would otherwise be necessary to achieve the requisite degree of silver halide deposition. This, of course, renders the procedure provided by the present invention highly desirable from an economical standpoint for the reasons more fully enumerated hereinbefore. In addition, the use of precipitating or flocculating agents can be dispensed with entirely according to the present invention since the use of the above described gelatin-polyoxyalkylenated adducts permits silver halide precipitation to be accomplished by merely changing the pH of the dispersion, i.e., rendering same acidic.

The dispersion thus formed, as pointed out hereinbefore, is available for effective use in photographic emulsion compositions. If desired, following precipitate formation, the dispersion may be washed preferably employing acid pH conditions and then re-dispersed in a suitable organic protective colloid vehicle such as unmodified gelatin. The washing operation may be repeated as often as is considered desirable although it is found that washings in excess of three or four are rarely necessary for achieving optimum results.

In carrying out the present invention, the silver halide is prepared in an aqueous solution of polyoxyalkylenated gelatin as the peptizing agent. The silver halide may be

prepared by any of the normal methods for the preparation of silver halide dispersions such as for example by introducing a stream of an aqueous solution of silver nitrate and a stream of an aqueous solution of at least one alkali metal halide preferably potassium bromide and potassium iodide into a constantly agitated solution of the peptizing agent. Alternatively however, the polyoxyalkylenated gelatin solution may be combined with one of the reactants, i.e., the nitrate or halide, and the other reactants may be introduced thereinto with stirring. Following silver halide precipitation, any ripening or digesting operations considered advisable may be effected. The dispersion of silver halide is then coagulated by lowering the pH of the solution to a value below 6 and preferably within the range of 2 to 4 and/or by the addition of flocculating agents of the type described above. The silver halide-polyoxyalkylenated gelatin dispersion forms granules and quickly settles from the liquid portion of the mass. The coagulum thus formed may be separated from the liquid by any one of several techniques such as for example by removing the supernatant mother liquor from the receptacle in which the mass is contained by means of a siphon or by decantation. For some types of emulsions the coagulum thus obtained may be used directly without any further treatment. However, where it is desired to further reduce the content of soluble salts which may be present, any one of several methods may be employed. For instance, the coagulum may be rinsed by treatment with cool water preferably with the pH thereof adjusted to approximate the range of the isoelectric point of the polyoxyalkylenated gelatin. As an alternative method, the coagulum may be redispersed in water made slightly alkaline using elevated temperatures; the solution is then stirred until redispersion of the coagulum is effected, following which the silver halide-polyoxyalkylenated gelatin dispersion may again be precipitated by addition of sufficient acid to reduce the pH to the coagulation point of the gelatin derivative. The foregoing procedure of redispersion and coagulation may be repeated as many times as is deemed necessary. Alternatively, the washing may be effected by reducing the pH to values below approximately 2 whereupon re-coagulation may be effected by the addition of a suitable alkaline material such as sodium or ammonium hydroxide.

The coagulum from which the water soluble salts have been removed, either by decantation or one of the methods described above, may then be redispersed in a suitable organic protective colloid such as gelatin, either modified or unmodified, to produce a composition suitable for use as a photographic emulsion. The pH values necessary for coagulation and redispersion depend in part on the dissociation constants of the ionic materials present in the silver halide dispersion and can, of course, vary over a wide range. In some cases, sedimentation will occur at any pH value although redispersion can be effected, for example, by the addition of a water-permeable organic colloid binder. Centrifugation, if necessary, can also be applied.

The emulsions of this invention may be coated onto various types of rigid or flexible supports, for example, glass, paper, metal, polymeric films of both the synthetic types and those derived from naturally occurring products, etc. Especially suitable materials include paper; aluminum; polymethacrylic acid methyl and ethyl esters; vinyl chloride polymers; polyvinyl acetals; polyamides such as nylon; polyesters such as the polymeric films derived from ethylene glycolterephthalic acid; and cellulose derivatives such as cellulose acetate, triacetate, nitrate, propionate, butyrate, acetate-propionate, or acetate-butyrate.

The light-sensitive material of the photographic emulsions comprises a compound of silver, for example, one or more of the silver halides of which silver chloride, silver bromide and silver iodide are examples. The preferred silver halide emulsion comprises a silver iodo-

bromide emulsion. It will be understood that preferred silver halide emulsions of varying halide concentration may be advantageously employed.

The invention will be illustrated in greater detail in conjunction with the following specific examples which set out representative preparations of the novel emulsions of this invention, which, however, is not limited to the details therein set forth and is intended to be illustrative only.

EXAMPLE I

900 grams of silver nitrate are dissolved in 5400 cc. of an aqueous ammoniacal solution and added over a period of 35 minutes to an aqueous solution of 22 grams of potassium iodide, 680 grams of ammonium bromide and 40 grams of a propylene oxide-gelatin reaction product. Approximately 35 milliliters of a 15 percent solution of poly-(sulfostyrene) is added and after a 5 minute digestion period, the pH is lowered by acid addition to effect coagulation of the dispersion. The coagulum thus obtained is washed four times at a low pH and 500 grams of an unmodified gelatin are added in solution with stirring. When the precipitation is dispersed, the solution is brought up to volume by gelatin addition. Preservatives are added, and the mass is digested at 61° C. with agitation while the necessary ripeners and stabilizers are added. The emulsion is then processed and coated as usual. The improvements provided by the present invention are clearly manifested by the fact that only one-third of the amount of poly (sulfostyrene) required in conventional emulsion preparation methods is necessary to achieve precipitation of the silver halide dispersion. Moreover, photographic elements prepared with samples of the emulsion of the above example are characterized by highly improved silver contents when compared to conventional photographic emulsion compositions.

EXAMPLE II

600 grams of silver nitrate in 470 cc. of distilled water are added over a period of 20 minutes to 1250 cc. of a previously prepared solution of 440 grams of potassium bromide, 24 grams of potassium iodide and 67 grams of a butylene oxide-gelatin reaction product. After a 3 minute digestion at 67° C. the pH is lowered by acid addition and 80 cc. of an 11 percent solution of poly (sulfostyrene) is added as a precipitating agent. After coagulation takes place, the precipitate is washed four times and redispersed in gelatin. This solution is brought up to volume by gelatin addition and digested while the necessary ripeners, stabilizers and preservatives are added. Results similar to those of Example I are obtained as regards the amount of precipitating agent required, and the silver halide-gelatin ratio characterizing the emulsion product.

EXAMPLE III

An emulsion is produced in the manner described in Example I, with the exception that an ethylene oxide-gelatin reaction product is used. Again, precipitation is effected with a minimal amount of precipitating agent. Results similar to those of the preceding examples are obtained.

EXAMPLE IV

An emulsion is made in the manner described in Example I, with the exception that acid ammonium sulfate is added after the digestion period as a precipitating agent. Results similar to those of the preceding examples are obtained.

Like results are obtained when the procedure of the foregoing examples is repeated using as polyoxyalkylenated gelatin derivatives the materials obtained by reacting gelatin with ethylene oxide, styrene oxide and cyclohexene oxide, i.e., precipitation was effected utilizing significantly reduced quantities of precipitating agent, while the silver halide dispersions produced there-

with displayed exceptional photographic properties in addition to significantly improved silver contents.

One of the salient advantages of the present invention is that the process of precipitating the silver halides in the presence of the polyoxyalkylenated gelatin eliminates the necessity of chilling and noodling the emulsion prior to the removal of the soluble salts by washing. This conventional method of chilling, noodling and washing necessitates the use of large amounts of water. There are at least three primary objections to such a procedure. One is that the water used for washing has to be quite pure and free of contamination and this necessitates elaborate and costly filtering operations. The second objection is that the noodles take up a considerable amount of the wash water and require higher concentrations of gelatin than would normally be necessary if this water was not absorbed. Thus, when conventional washing methods are employed emulsions have to be made with at least a 4 percent gelatin content whereas the instant process requires considerably less gelatin, e.g., of the order of 1.5 to 2.5 percent. In large manufacturing operations this involves considerable savings. The third objection is that the high water content of the conventionally washed emulsions militates against using higher coating speeds which in turn necessitates faster drying means. A further disadvantage of the conventional emulsion making method is that the silver nitrate solutions can only be used in limited concentration, that is the volume of solution must be kept small as determined by the gelatin content whereas in the instant process higher volumes and less concentrated solutions can be used since all the liquid is removed in the precipitation. This larger choice of solution volume may in turn allow greater control of photographic characteristics, i.e., grain size, etc.

A further advantage of the invention is that it allows one to make gelatin emulsions with low gelatin content since substantially all of the water used in making the emulsion is removed from the precipitated emulsion. Since practically no solvent is required for redispersion, the gelatin concentration for coating can be easily controlled by the addition of water. When noodled emulsions are washed by the conventional procedure the minimum concentration required for proper setting of the emulsion is approximately 4 percent. In order to maintain this percentage as well as the silver halide/gelatin ratio required for the finished film, the formulae and procedures are sometimes hampered by serious operational limitations. During the conventional washing operation the water content of the emulsion is increased while substantially all of the water can be removed by precipitation. This offers the simple means of increasing the solids content of the emulsion after they have been made. Thus, one can obtain emulsions that have a higher silver halide/gelatin ratio than those obtained with emulsions which have been washed by the conventional method.

The emulsions of the present invention may be chemically sensitized by any of the accepted procedures. For example, the emulsions may be digested with naturally

active gelatin or sulphur compounds can be added. Chemical sensitization may also be effected by the use of noble metal salts, reducing agents and the like. Optical sensitization may be effected by the use of cyanine and merocyanine dyes, etc.

Other conventional additives such as speed-increasing agents, anti-foggants, restrainers, accelerators, preservatives, coating aids and/or stabilizers may also be included in the emulsion compositions of the present invention.

Various modifications of the present invention as set forth in the preceding examples will become apparent to those skilled in the art such as the use of equivalent materials not necessarily disclosed in the specification. It is not intended, therefore, that the invention be limited except as necessitated by the appended claims.

What is claimed is:

1. A method of preparing a silver halide dispersion comprising the steps of mixing together a water soluble silver salt and at least one water soluble halide salt in the presence of a polyoxyalkylenated derivative of gelatin to form thereby a dispersion of silver halide and said polyoxyalkylenated gelatin derivative, coagulating and recovering the dispersion thus formed.

2. A method according to claim 1 wherein the polyoxyalkylenated gelatin-silver halide coagulum thus recovered is redispersed in a protective colloid therefor.

3. A method according to claim 2 wherein the protective colloid is gelatin.

4. A method according to claim 2 wherein the polyoxyalkylenated gelatin-silver halide coagulum thus recovered is washed prior to redispersing same in the said protective colloid therefor.

5. A method according to claim 1 wherein the polyoxyalkylenated gelatin derivative is the reaction product of gelatin with a compound selected from the group consisting of ethylene oxide, propylene oxide, butylene oxide, styrene oxide, cyclohexene oxide and mixtures thereof.

6. A method according to claim 1 wherein coagulation is effected by reducing the pH of the silver halide dispersion to a value below 6.

7. A method according to claim 1 wherein coagulation is effected by the addition of poly(sulfostyrene) to the silver halide dispersion.

8. A method according to claim 1 wherein coagulation is effected by the addition of acid ammonium sulfate to the silver halide dispersion.

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