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PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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This invention relates to photographic light-sensitive emulsions and their preparation, and more particularly silver halide emulsions in which a polymeric compound prepared by the interpolymerization of acrylic or alpha-substituted acrylic acids with their amides is used as the carrier or protective colloid for the light-sensitive agent.

Heretofore, gelatin has been universally employed as the carrier for the light-sensitive silver halide in photographic emulsions. However, this substance has numerous disadvantages and it has been long sought to obtain a substitute therefor which possesses the advantages of gelatin with the minimum of its disadvantages. Many materials have already been proposed for this purpose. Among these are polyvinyl alcohol alone or in combination with other substances, partially hydrolyzed polyvinyl esters, polyvinyl acetals, partially hydrolyzed cellulose esters, regenerated cellulose, water-soluble polyamides and others. However, in spite of the numerous substances suggested, gelatin still remains the protective colloid employed in photographic emulsion manufacture.

The characteristics of gelatin which have made it so far the universal protective colloid employed in the manufacture of silver halide emulsions are its ability to hold light-sensitive silver halides in finely divided state, its good permeability to water, the insolubility of its gels in water and the photographic developing, fixing and other baths conventionally used in the processing of photographic elements, and its ability to form a thin coating of the light-sensitive emulsion upon the various materials used for supports, such as film, paper, glass, and metal plates.

However, being a natural product, one of the most serious drawbacks of gelatin is its extremely variable properties which depend upon its history or source. Thus, a batch of gelatin obtained from one locality will differ in properties from that obtained in another locality. Moreover, gelatin is susceptible to the action of mold and bacteria. Then to obtain the highly purified gelatin required for photographic purposes necessitates expensive and numerous refining procedures.

The desirability of synthetic material which possesses the advantageous properties of gelatin

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and which can be exactly duplicated so that a material of predetermined and standardized properties without differences in different batches is always obtained has long been recognized and such a gelatin substitute has long been sought by photographic manufacturers. Thus far among the many substitutes proposed, none apparently has met all the requirements for a protective colloid useful for practical photographic silver halide emulsions.

Accordingly, a primary object of our invention is to provide a synthetic carrier or protective colloid capable of duplication which may be used in the manufacture of photographic light-sensitive emulsions.

Another object of our invention is to provide such a synthetic material which possesses many of the advantageous properties of gelatin without its many disadvantages.

Still another object of our invention is to provide a synthetic material having the property of thermal-reversible gelation under certain conditions. By this we mean that an aqueous solution of the material will set under certain conditions to form a gel, which gel is convertible into a liquid when heated, but on cooling, again forms a gel.

It is another object of our invention to provide a carrier capable of forming firm, strong gels in an aqueous medium.

A still further object is to produce a photographic emulsion which when applied to a suitable base forms a coating of unusual resistance to abrasion without requiring any hardening treatment, such as is required for gelatin containing emulsions.

We have discovered that interpolymerization products of acrylic and alpha-substituted acrylic acids with their amides in suitable proportions serve as a basis for the formation of protective colloids which exhibit the phenomenon of forming thermal-reversible gels in aqueous media. The exact properties of the synthetic substance are determined in part by the ratio of free acid to the amide in the polymerization mixture. Also affecting the properties are the pH of the aqueous medium in which the polymer is dissolved, as well as the presence or absence of certain metal ions, such as the alkali and alkaline earth metal salts of the polymeric substance.

The preferred pH range to produce desirable gelling properties for various compositions of methacrylic acid and methacrylic amide interpolymers is indicated in the following table. The parts are by weight.

Composition of Interpolymer		Preferred pH Range
Acid	Amide	
25	75	4.5–7.0
50	50	5.0–6.5
75	25	6.0–6.5

The addition of metal ions, such as aluminum and chromium tends to reduce the solubility and harden the gel.

The properties of the interpolymeric substances may be further varied through wide ranges by the incorporation into the polymer molecule of other interpolymerizable vinyl compounds, as for example, esters of acrylic acid or vinyl esters, such as acrylic acid methyl ester and vinyl acetate.

Alcohol groups may be introduced into the acrylic acid-acrylamide polymerization mixture by incorporating vinyl esters capable of interpolymerization and then subsequently hydrolyzing or partially hydrolyzing the polymer by well-known hydrolysis methods, such as used in preparing polyvinyl alcohol from polyvinyl acetate and other esters. This increases the permeability of the gel formed to water and photographic processing solutions. The strength of the gel and the tendency to form gel structures may be increased by increasing the ratio of certain groups which exhibit strong attractive forces, such as hydroxyl, amino, amide, formyl, carboxyl, nitrile, and similar polar groups.

It is also possible to control the viscosity of the solutions of given strength of the interpolymer, at least in part, by varying the polymerization conditions by well-known methods, to increase or decrease the molecular weight of the polymer produced, such as by varying the amount of the catalyst, the temperature, or the proportions of the monomers. Thus, a high concentration of catalyst or a high temperature results in a low molecular weight interpolymer and low viscosity solutions. Use of a low catalyst concentration and low temperature gives the reverse effects.

The viscosity as well as the tendency to form gels may also be controlled by certain after treatments of the polymer. Thus, if the polymer is one containing free carboxyl groups, then these may be partially esterified with a polyhydric alcohol, such as ethylene glycol or glycerol. On the other hand, if the polymer contains hydroxyl groups, esterification with a polybasic acid produces a similar effect.

One of the particular advantages of the interpolymers of the acrylic and alpha-substituted acrylic acids with their amides is that they may be utilized in a manner similar to that in which gelatin is employed in making up photographic emulsions and layers.

The interpolymer may be dissolved in hot water made slightly alkaline with any suitable alkali, such as sodium, potassium, or ammonium hydroxides or carbonates, so that a solution having a pH of from about 4.5–7 is formed. This may then be added to the usual light-sensitive materials, suspended in a small amount of gelatin. For example, about 1 to 3% of gelatin solution which is only a small part of that heretofore required to make a photographic gelatin emulsion is used.

While the mass is still liquid at the elevated temperature, it is coated on a suitable support and chill-set, thus forming a thin, hard, scratch-resistant coating of the light-sensitive emulsion, which may be treated with developing and fixing solutions and subsequently washed with water without dissolution. Our interpolymerization products holds the light-sensitive silver halides in finely divided state. The silver halide does not appreciably clump or coagulate when added to the solution. Preliminary dispersing of the silver halide in a so-called "silver halide dispersing agent" before mixing it with the solution of the interpolymer is not required.

Our interpolymers are most advantageously used with standard photographic emulsions to replace a considerable part of the gelatin heretofore required. Thus, the silver halide salts may be first prepared from the usual alkali metal halide salts, such as ammonium bromide, potassium iodide, potassium bromide, potassium chloride, sodium chloride, and silver nitrate in a 2 or 3 per cent aqueous gelatin solution, and to this is then added a solution of our interpolymeric product having a pH of about 4.5–7. We have found that our interpolymeric product increases the viscosity of the gelatin. Thus, less gelatin than heretofore required is used with the highly advantageous result that thinner coatings can be produced. An additional important advantage is that a greater silver-to-colloid ratio is attained than is possible with gelatin alone. This advantage is of especial significance in the production of X-ray film, since the larger ratio of silver made possible in our emulsion provides for greater contrast in the film. Another advantage which we have found is that the presence of the gelatin plasticizes the interpolymer mixture and serves to form a good adhesion between the emulsion and the support on which it is coated.

Photographic supports coated with our novel photographic emulsion may be exposed, developed, fixed, and washed in the usual baths to produce a photographic image. However, a hardening bath or hardening agent is unnecessary since the coating containing our polymeric product is not dissolved by these treatments and exhibits an unusual resistance to abrasion or scratching without any hardening treatment.

The following examples illustrate the preparation of our interpolymeric product:

Example 1

20 grams each of methacrylic acid and methacrylamide are dissolved in 100 cc. of distilled water and 0.1 gram of benzoyl peroxide is added as the polymerization catalyst. This mixture is heated to 70°–90° C. for about ½ hour, after which time, an insoluble polymer has precipitated. This material may be redissolved in hot water made slightly alkaline with a few drops of a 5% ammonium hydroxide or sodium hydroxide solution so that the pH of the solution of the polymer is about 5–6.5. The solution upon cooling sets to a firm, strong gel at a temperature of about 35–45° C. This gel is thermal-reversible, that is, on heating it melts to form a liquid and when cooled again forms the gel. The exact melting temperature depends partly upon the concentration of the solution and partly on the pH of the mixture. The melting point may also be

changed by varying the ratio of amide to acid in the original mixture.

This interpolymer is compatible with aqueous gelatin solutions in all proportions.

Example 2

15 grams of methacrylic acid, and 15 grams of methacrylamide, and 5 grams of methylacrylate are added to 100 cc. of distilled water and 0.1 gram of benzoyl peroxide are added to the mixture as a polymerization catalyst. Upon heating to 60° C. or higher, a homogeneous solution is obtained which polymerizes to form a water-insoluble product. However, solutions of this material may be prepared as in Example 1 by redissolving in hot water made slightly alkaline and on cooling forms gels which are thermal-reversible. In this case, when photographic emulsions are prepared and cast on a suitable support, the dried film formed is firmer and tougher than those formed from the product obtained in Example 1.

Example 3

A solution was prepared containing equal parts by weight of an 8% solution of the polymer prepared in Example 1 and a solution of polyvinyl alcohol of the same strength by mixing the two at 40°–50° C. On cooling, the mixture was found to set to a gel which is thermal-reversible, unlike solutions of polyvinyl alcohol alone which are not thermal-reversible. The gel has an increased permeability to water, so that is is more rapidly penetrated by developing, fixing, and washing solutions.

Example 4

40 grams each of methacrylic acid and methacrylamide are added to 300 cc. of water in the presence of 0.1 gram of benzoyl peroxide. The mixture is heated for several hours at 85–90° C. until slight precipitation and an increase in viscosity occurs. Then 300 cc. of water is added and the heating is continued at the same temperatures until a further increase in viscosity occurs. Then an additional 300 cc. of water is added and the heating continued until a gel-like material is formed.

This product is dissolved in twice its weight of 0.2 N sodium hydroxide solution at room temperature and the material precipitated from its solution by adding 0.2 N sulfuric acid. The filtered material may be washed with organic solvents, such as acetone to remove any residual catalyst if desired, which, if present, may fog the photographic emulsion.

The washed material is then dissolved in 0.2 N sodium hydroxide and brought to a pH of from 6–7, by addition of a dilute solution of any suitable acid, as for example, sulfuric acid, acetic or methacrylic acid. This solution will set to a thermal-reversible gel. However, in preparing a photographic emulsion, the solution may be added directly to a photographic emulsion containing gelatin, as for instance, any of those mentioned in Examples 5, 6, 7, and 8, in sufficient amount to bring the viscosity of the emulsion to that suitable for coating.

Example 5

A 2% solution of a polymer prepared as described in Example 1 is heated to about 40° C. and there is added thereto with rapid stirring an aqueous solution containing about 3% of gelatin and potassium iodide, potassium bromide, and silver nitrate in amounts usually employed in

preparing standard photographic emulsions to precipitate the silver halide. The emulsion is then coated on a suitable base such as a glass plate.

The coated plate may be exposed and developed in any of the customary photographic developers and fixed in the usual manner to produce a photographic image.

Example 6

Equal parts by volume of a standard photographic emulsion prepared in about a 2% gelatin solution and a 1% solution of a polymer prepared as described in Example 4 were mixed in the dark at 40° C. and coated on a glass plate. The gelatin acts as a plasticizer for the mixture and further imparts great adhesion between the mixture and the glass. The coated plate may now be exposed, developed in any suitable developer, such as metol-hydroquinine carbonate developer (Ansco 47) and fixed in the usual manner to produce a photographic image. The coating so produced is unique in its unusual resistance to abrasion without any subsequent hardening treatment.

Example 7

Into a 3% solution of a polymer as described in Example 2 there are incorporated potassium bromide and silver nitrate and about 2% of gelatin. The mixing takes place at a temperature of about 40° C., and the product obtained is then cast on a suitable base. The dried film which is formed is tougher than that obtained in Examples 3, 4, and 5.

Example 8

An emulsion is prepared as in Example 7, except that for the interpolymer therein, there is substituted an 8% solution of the product described in Example 3. The light-sensitive elements are incorporated in the solution by mixing at a temperature of about 40–50° C. After casting the solution on a suitable support and cooling, a thin, firm coating is obtained with increased permeability to aqueous solutions used for processing.

As pointed out above, the melting point of the interpolymer gel may be changed by varying the ratio of amide to acid in the polymerization mixture. Accordingly, what ratios will be used will depend on the melting point desired in the final product. Likewise, the addition of the acrylic acid and vinyl esters to the interpolymerization mixture will be varied in accordance with the amount of strength that is desired in the final product. Such considerations also apply with respect to the amount of poplyvinyl alcohols employed or other compounds containing groups which exhibit strong attractive forces. In this case, the amounts added will depend on the desired amount of permeability of the gel to water and the desired amount of gel-forming properties in the final product.

With respect to the preparation of the interpolymer of acrylic acid and alpha-substituted acrylic acid with their amides, in addition to methacrylic acid and methacrylic amide mentioned in the examples, there may also be used acrylic acid and acryl amide, alpha-phenyl acryl-amide, alpha-chloroacryl amide and the other alpha-substituted acrylic acids and acryl amides.

In addition to benzoyl peroxide as a catalyst for the interpolymerization action, there may be used other catalysts, such as ammonium persulfate, sodium perborate, percarbonic and perphosphoric acid, hydrogen peroxide, ozonides, or other com-

pounds which release oxygen, and controlled amounts of atmospheric oxygen. The catalyst is generally used in small amounts, ranging from about 0.01 to 2% by weight of the polymerizable organic compounds. About 0.2% has been found desirable in most instances. The temperature at which the polymerization may be carried out may range from about 20–100° C., although 60–90° C. is preferred.

While the preferred pH of the solution of the interpolymeric product is from about 4.5 to approximately 7, we have found that a range of from about 4–9 is also suitable. If the solution becomes too acid, the interpolymer will precipitate therefrom and not gel. If the solution is too alkaline, it will not form a gel but remain dissolved. However, when the pH of the solution is controlled within the range above set forth gelation thereof takes place. Only a few drops of an alkaline solution are necessary to impart the desired pH to the solution. For this purpose a 5% solution of either ammonium hydroxide, sodium hydroxide, or potassium hydroxide may be used as well as solutions of any alkali metal hydroxides and carbonates.

The effect on the viscosity of gelatin solutions is shown by the following: The flow time in seconds through the test viscosimeter of a standard type of a photographic gelatin of 10% concentration in water alone at 40° C. was found to be 50 seconds. Using a 2% solution of the same gelatin in water, the flow time was only 24.8 seconds. However, when 0.08% of the interpolymer described in Example 4 was added to the 2% solution, the flow time thereof was increased to 47.3 seconds, or was nearly equal to that of the 10% gelatin solution. When adding .16% of the interpolymer to the 2% gelatin solution, the flow time was increased to 115.6 seconds. The pH of the mixture was adjusted to 6 in these measurements. Thus it will be seen that a large amount of the gelatin heretofore required in preparing photographic gelatin emulsion of the necessary viscosity for coating is eliminated by small amounts of our interpolymers.

Another advantage of our invention is that it makes possible the use of gelatin which produces such low viscosity solutions that are not in themselves suitable for photographic use, since the addition of only a small amount of our interpolymers imparts the required viscosity for coating operations.

In addition to the silver halides as light-sensitive compounds, there may also be used light-sensitive chromates, such as potassium bichromate, iron salts, and diazo compounds.

As will be seen, our emulsions have many advantages over the gelatin alone as a protective colloid. While possessing the physical and photographic properties of gelatin, they always possess the same chemical properties and may be reproduced exactly so that one always has available a standard product possessing standard properties. Like gelatin, the products are soluble in warm water and not in cold so that they may be washed and processed as an ordinary gelatin silver halide coating. Likewise, their properties may be adjusted to any predetermined standard.

We claim:

1. A light-sensitive photographic emulsion which comprises a silver halide dispersed in gelatin and a thermal-reversible gel comprised of the interpolymer of an acrylic acid with an acrylic acid amide, the amount of said interpolymer being at least 4% of the amount of gelatin, and said interpolymer containing at least 25% of said acid and at least 25% of said amide.

2. A light-sensitive photographic emulsion which comprises a silver halide dispersed in gelatin and a thermal-reversible gel composed of the interpolymer of an acrylic acid with an acrylic acid amide, the amount of said interpolymer being at least 50% of the amount of gelatin, and said interpolymer containing at least 25% of said acid and at least 25% of said amide.

3. A light-sensitive photographic emulsion which comprises a silver halide dispersed in gelatin and a thermal-reversible gel composed of the interpolymer of methacrylic acid and methacrylamide, the amount of said interpolymer being at least 4% of the amount of gelatin, and said interpolymer containing at least 25% of said acid and at least 25% of said amide.

4. A light-sensitive photographic emulsion which comprises a silver halide dispersed in gelatin and a thermal reversible gel composed of the interpolymer of methacrylic acid, methacrylamide, and methylacrylate, the amount of said interpolymer being at least 4% of the amount of gelatin, and said interpolymer containing at least 25% of said acid and at least 25% of said amide.

5. A light-sensitive photographic emulsion which comprises a silver halide dispersed in gelatin and a thermal-reversible gel composed of an interpolymer of methacrylic acid, methacrylamide and polyvinyl alcohol, the amount of said interpolymer being at least 4% of the amount of gelatin, and said interpolymer containing at least 25% of said acid and at least 25% of said amide.

6. A light-sensitive photographic emulsion which comprises a silver halide dispersed in gelatin and a thermal-reversible gel comprised of the interpolymer of an acrylic acid with an acrylic acid amide, the amount of said interpolymer being at least 4% of the amount of gelatin, and said interpolymer containing at least 25% of said acid and at least 25% of said amide, said gel having a pH in aqueous solution of from about 4 to about 9.

7. A light-sensitive photographic emulsion which comprises a silver halide dispersed in gelatin and a thermal-reversible gel composed of the interpolymer of an acrylic acid with an acrylic acid amide, the amount of said interpolymer being at least 4% of the amount of gelatin, and said interpolymer containing at least 25% of said acid and at least 25% of said amide, said gel having a pH in aqueous solution of from about 4.5 to about 7.

8. A photographic material which comprises a light-sensitive layer comprising a silver halide dispersed in gelatin and a thermal-reversible gel composed of the interpolymer of an acrylic acid with an acrylic acid amide, the amount of said interpolymer being at least 4% of the amount of gelatin, and said interpolymer containing at least 25% of said acid and at least 25% of said amide.

9. A method of preparing a light-sensitive photographic emulsion which comprises dispersing a silver halide at a temperature of at least 35° C. in an aqueous solution having a pH of from about 4 to about 9 and containing gelatin and a gel-forming interpolymer of an acrylic acid with an acrylic acid amide, the amount of said interpolymer being at least 4% of the amount of gelatin, and said interpolymer containing at least 25% of said acid and at least 25% of said amide, and lowering the temperature of said solution to form a gel.

10. A method of preparing a light-sensitive pho-

tographic emulsion which comprises dispersing a silver halide at a temperature of at least 25° C. in an aqueous solution having a pH of from about 4.5 to about 7 and containing gelatin and an interpolymer of methacrylic acid and methacrylamide, the amount of said interpolymer being at least 4% of the amount of gelatin, and said interpolymer containing at least 25% of said acid and at least 25% of said amide, and lowering the temperature of said solution to form a gel.

11. A method of preparing a light-sensitive photographic emulsion which comprises dispersing a silver halide at a temperature of at least 35° C. in an aqueous solution having a pH of from about 4.5 to about 7 and containing gelatin and an interpolymer of methacrylic acid, methacrylamide, and methylacrylate, the amount of said interpolymer being at least 4% of the amount of gelatin, and said interpolymer containing at least 25% of said acid and at least 25% of said amide, and lowering the temperature of said solution to form a gel.

12. A method of preparing a light-sensitive photographic emulsion which comprises dispersing a silver halide at a temperature of at least

35° C. in an aqueous solution having a pH of from about 4.5 to about 7 and containing gelatin and an interpolymer of methacrylic acid, methacrylamide, and polyvinyl alcohol, the amount of said interpolymer being at least 4% of the amount of gelatin, and said interpolymer containing at least 25% of said acid and at least 25% of said amide, and lowering the temperature of said solution to form a gel.

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