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PHOTOGRAPHIC SILVER HALIDE
EMULSIONS

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This invention relates to photographic silver halide emulsions which comprise a silver halide dispersed in a thermal-reversible gel composed of a polyvinyl alcohol which is mixed with a gelling amount of a water-soluble nitrogenous substance, such as water-soluble proteins, protein degradation products, and alpha-amino acids.

By the terms "thermal-reversible gel" we have reference to a gel which on heating becomes liquid and on cooling again becomes a gel. By the term "polyvinyl alcohol" we include not only polyvinyl alcohol polymers, but other polymeric vinyl compounds which contain hydroxy groups, such as partially hydrolyzed polyvinyl acetate, polyvinyl propionate, polyvinyl butyrate, polyvinyl propionaldehyde acetals, polyvinyl butyraldehyde acetals, and polyvinyl ethers, such as polymers of alkyl and aryl vinyl ethers. By our process any water-soluble polyvinyl alcohol can be converted into a thermal-reversible gel suitable as a carrier or protective colloid for light-sensitive silver salts.

The protective colloid in which the light-sensitive silver halide grains are suspended must keep the grains of silver halide finely dispersed in the emulsion in order to eliminate clumping and eventual graininess in the photographic image. The colloid must also be stable over a long period of time so that both the undeveloped and the processed emulsion are of good permanence. Likewise, the protective colloid must not impart photographic characteristics to the light-sensitive particles which are undesirable. In addition, the carrier must be such that it can be simply handled and yet be accurately reproduced so that the emulsions can be prepared and applied in the form of coatings in practical methods. Another important requirement of the colloid is that it must permit the penetration of treating solutions without adversely affecting its strength, toughness and permanence.

Gelatin has universally been used as a protective colloid for light-sensitive silver halides in such emulsions because it satisfies most of the above-mentioned requirements. However, gelatin has certain disadvantages which it has long been sought to overcome. Being a natural product, one of its most serious drawbacks is the variation in the properties of different batches. Thus, a batch of gelatin obtained from one locality will differ in properties from that obtained in another. Moreover, gelatin is susceptible to the action of bacteria. In order to obtain the highly purified gelatin required for photographic purposes, there is necessitated expensive and numerous refining procedures.

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The desirability of a synthetic material which possesses the advantageous properties of gelatin and which can be exactly reproduced so that a material of predetermined and standardized properties, without differences in different batches, is always obtained has long been recognized and a gelatin substitute has long been sought by photographic manufacturers. Among the many substitutes proposed, however, none has apparently met the requirements for a protective colloid for practical photographic emulsion manufacture. Extensive research for the development of emulsion media better than gelatin has as yet failed to produce a satisfactory substitute. Among the materials which have been suggested for this purpose are partially hydrolyzed polyvinyl esters, polyvinyl acetate, partially hydrolyzed cellulose esters, regenerated cellulose, water-soluble polyamides, cellulose nitrate and polyvinyl alcohol, alone, or in combination with other substances.

An important practical disadvantage of polyvinyl alcohol as a direct substitute for gelatin in photographic emulsions is the failure of its aqueous solutions to exhibit the phenomenon of thermal-reversible gelation. This property is one of great importance in the manufacture of photographic emulsions, since it makes possible the removal of soluble salts by washing in cold water and also permits coating of the emulsion on the support by simply heating the gel until it melts to a liquid. It is for this reason that various substances have been added to polyvinyl alcohol to impart the property of thermal-reversible gelation.

It is an object of our invention to provide a photographic emulsion which contains a protective colloid possessing the property of thermal-reversible gelation in aqueous solution and which may be used as a substitute for gelatin.

Another object of our invention is to provide a photographic emulsion which contains a substance capable of duplication and possessing standardized properties which may be used as a protective colloid for the silver halide salts in place of gelatin.

A still further object of our invention is to provide a carrier for silver halide photographic emulsions which serves as a substitute for gelatin and is capable of modification to give emulsions having a wider range of physical properties than is possible with gelatin.

We have discovered that water-soluble proteins and protein degradation products, such as casein, albumin, gelatin and glue, as well as certain alpha-amino acids and their condensation

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products, such as diketopiperazines, when added to aqueous solutions of polyvinyl alcohols impart the property of thermal-reversible gelation.

The photographic emulsions of our invention may be prepared by merely adding to an aqueous solution of a polyvinyl alcohol, aqueous solutions of alkali metal halides conventionally used for producing the light-sensitive silver salt and silver nitrate. To this mixture may be then added a gelling amount of the water-soluble nitrogenous compound which is to be used as the gelling agent. In an alternative procedure, the alkali metal halides are added to a solution of polyvinyl alcohol and this mixture is then removed to a dark room where there is added a solution of silver nitrate containing a small amount of the water-soluble nitrogenous compound.

The emulsion thus formed is dried. On adding water it swells to form a gel from which the soluble salts are washed out. This gel may then be melted and the viscous melt formed is then coated on any suitable support, such as glass, paper, or films made of cellulose derivatives.

On drying, a tough film, which is especially scratch-resistant, is formed. Upon exposure and development by the usual photographic technique, images of good quality are produced.

The following examples are illustrative of our invention:

Example 1

To 10 parts by weight of a 10% aqueous solution of far-hydrolyzed polyvinyl acetate having a viscosity of 20 centipoises in 4% solution was added one part of glycine. This mixture was then heated to boiling for a few minutes, and spread out to dry at a temperature ranging from about 20–60° C. The dried material, although insoluble in cold water, swells therein to form a tough gel which is thermal-reversible. Upon warming, the gel melts and may be coated on glass or other supports to form, after drying, a clear colorless, tough film, which is especially scratch-resistant.

Example 2

8.5 parts by weight of a far-hydrolyzed polyvinyl acetate of medium viscosity and 1.5 parts of gelatin were dissolved in 80 parts of hot water and the solution spread out to dry at room temperature. The dried material, although insoluble in cold water, swells therein to form a tough gel which is thermal-reversible. This gel may be washed in cool water for long periods of time without dissolving. The washed gel is thermal-reversible and may be melted and cast to form a colorless, tough, scratch-resistant film on drying. The dried film is completely transparent and homogeneous. When more than 20% of gelatin was added, however, the resulting dried films are no longer transparent, but resemble coarse ground glass in appearance. Mixtures of such concentrations are not compatible.

Example 3

1 part by weight of bone glue was added to 9 parts of the 10% solution of polyvinyl alcohol described in Example 1. The mixture was heated for a few minutes until the glue had dissolved and the solution spread out to dry at room temperature. Although insoluble in cold water, the dried material swells therein to form a gel. This gel is also thermal-reversible.

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Example 4

To 55 cc. of a 14% aqueous solution of a medium viscosity polyvinyl alcohol (containing less than 5% by weight of acetate calculated as vinyl acetate) was added a solution of 5 grams of potassium bromide and 0.3 gram of potassium iodide dissolved in 15 cc of water. The mixture was then removed to a dark room and to it was added, over a period of two minutes with vigorous stirring, a solution of 5 grams of silver nitrate dissolved in 15 cc. of a 10% gelatin solution. The emulsion is spread out to dry at room temperature. The dried material is then swollen in cool water to form a gel from which the water-soluble salts are washed out. This gel was then melted on a water bath and coated on glass, paper, and cellulose derivative supports. Upon exposure and development by the usual photographic procedures, images of good quality were produced.

Example 5

In 15 cc. of a 3% gelatin solution there is added 15 cc. of an aqueous solution containing 5 grams of potassium bromide and 0.3 gram of potassium iodide. To this mixture is then added a solution of 5 grams of silver nitrate dissolved in 15 cc. of water to precipitate the silver halide. To this is then added 55 cc. of a 20% aqueous solution of medium viscosity polyvinyl alcohol (containing less than 5% by weight of acetate calculated as vinyl acetate), and the mixture vigorously stirred. The mixture is then spread out to dry at room temperature. The dried material is swollen in cool water to form a gel from which the water-soluble salts are washed out. This gel is then melted by heating and coated on a transparent cellulosic film. Upon exposure and development by the usual photographic procedures, images of good quality were produced.

Example 6

The same procedure was followed as in Example 4, except that an equivalent amount of bone glue was substituted for the gelatin. The emulsion so obtained when coated, exposed, and processed gave fine quality images. The coating was found to be somewhat more sticky than in that of Example 4.

Example 7

120 cc. of a 10% solution of polyvinyl alcohol of medium viscosity (as in Example 4) is diluted with 140 cc. of water. The following solutions are then run in with rapid stirring through the time of addition:

A

40 cc. of a 50% solution of silver nitrate

B

12.8 grams of potassium bromide,
3 grams of potassium chloride,
0.5 gram of potassium iodide, and
40 cc. of water.

200 cc. of a 10% solution of polyvinyl alcohol is then added and the emulsion stirred until well mixed, at a temperature of 40° C. There is then added 16 cc. of a 10% gelatin solution. The resulting mixture is then spread out to dry at room temperature. The dried material is then swollen in cool water to form a gel from which the water-soluble salts are washed out. This gel is then melted and coated, the same as set forth in Example 4.

Example 8

3 grams of the dried polyvinyl alcohol-gelatin product obtained according to Example 2 is swollen and dissolved by heating at about 50° C. in 80 cc. of water. To this solution is added a solution of 5 grams of potassium bromide and 0.3 gram of potassium iodide in 20 cc. of water. The solution is cooled to about 40° C. and with vigorous stirring a solution of 5 grams of silver nitrate in 15 cc. of water is added. 15 grams of the dried polyvinyl alcohol-gelatin product which is swollen with water is then added. The emulsion is then spread out to dry and the dried material is then swollen in cold water and the soluble salts removed therefrom. After melting by heating, the viscous liquid obtained is coated on a suitable support, and permitted to chill set.

Example 9

The procedure is the same as in Example 8 but instead of starting with the dried polyvinyl alcohol-gelatin product, one starts with a solution containing 2.6 grams of polyvinyl alcohol and 0.5 gram of gelatin dissolved in 80 cc. of water.

In general, only small amounts of the nitrogenous gelling agents are required and, in fact, larger amounts are, as a rule, incompatible with the polyvinyl alcohol and give films which resemble coarse ground glass in appearance. While these incompatible mixtures might be useful for some purposes, especially when the added substance is dispersed in the polyvinyl alcohol solution, we prefer to utilize those compositions which are compatible and form transparent films on drying. The amount of water-soluble nitrogenous substances which is added to the polyvinyl alcohol solution need only be sufficient to cause gelling. In general, the amount added may range from about 1% to about 20%, based on the weight of the polyvinyl alcohol, where transparent films are to be obtained. Where opaque films are desired, the amount may vary from above 20% to about 98%. Heating facilitates solution of the ingredients in the mixture.

The exact physical properties of the photographic emulsion, made according to our process, may be varied to some extent, not only by the nature and the amount of the added nitrogenous substance, but also by varying the molecular weight, degree of hydrolysis, and nature of the other substituents of the polyvinyl alcohol employed. If, for example, a polyvinyl acetate of high molecular weight is hydrolyzed as, for example, according to the process of the Skirrow Patent No. 1,971,951, to yield a polyvinyl alcohol, solutions containing this product will be more viscous than those of equal concentration containing a polyvinyl alcohol prepared from a lower molecular weight polyvinyl acetate. In this case, a smaller proportion of the gelation agent is employed than in the case when a polyvinyl alcohol of lower molecular weight is employed as the protective colloid.

The degree of hydrolysis of the polyvinyl ester also contributes to the physical properties of the polyvinyl alcohol formed and, therefore, is an important factor in determining the characteristics of the aqueous solutions and the gels obtained therefrom. Also playing a part in the gelling characteristics of the solution of the protective colloid is the nature of the unhydrolyzed groups. Thus, for example, if a polymer of vinyl formate is partially hydrolyzed to produce a polyvinyl alcohol, the properties of this product will

differ from those of a similar product made from a polymer of vinyl acetate. The formyl groups have a greater tendency to exert attractive forces of the so-called "secondary valence" type on one another, thereby increasing the tendency to gel and the strength of the resulting gel due to the improved cohesive properties present in such a polymer.

Other substituted groups may be present in the polyvinyl alcohol molecule. Thus, such polyvinyl alcohols fall within the scope of this invention which are produced by hydrolyzing an interpolymer of a vinyl ester with other vinyl compounds, such as nitriles, esters, amides and similar derivatives of acrylic and alpha-substituted acrylic acids, as well as the free acids themselves.

The water-soluble protein degradation products which we use as gelation agents may be produced in any well known manner, as for example, according to the processes set forth in United States Patents Nos. 1,719,711, 1,727,866, and 1,815,983, that is, by either acid or alkaline hydrolysis.

In addition to the silver halides, other photosensitive substances, well known in the photographic art, may be employed, as for example, chromates, iron salts, diazo compounds, and the like.

It will thus be seen that our invention provides photographic emulsions which have outstanding advantages over emulsions containing gelatin and the like. Thus, they may be prepared with definite purity and standardized properties which can be reproduced at all times, as contrasted with gelatin emulsions whose properties may vary in marked degree due to the differences that exist in different batches of the gelatin.

We claim:

1. A method of preparing a light-sensitive photographic emulsion in the form of a thermal-reversible gel, suitable for sensitizing photographic materials and adapted to form a film of tough, transparent colloid having a light-sensitive silver halide dispersed therein, which consists in preparing a dispersion of a light-sensitive silver halide in an aqueous solution of a polyvinyl alcohol which contains, as the sole gelling agent therefor, a gelling amount from about 1% to about 20% by weight of the amount of polyvinyl alcohol, of a water-soluble nitrogenous compound selected from the group consisting of proteins, protein degradation products, alpha-amino acids and their condensation products, evaporating the resulting dispersion to dryness and swelling the dried composition thus obtained in cold water, whereby the product is converted to a gel and any water-soluble salts contained therein are washed out.

2. A method of preparing a light-sensitive photographic emulsion in the form of a thermal-reversible gel, suitable for sensitizing photographic materials and adapted to form a film of tough, transparent colloid having a light-sensitive silver halide dispersed therein, which consists in preparing a dispersion of a light-sensitive silver halide in an aqueous solution of a polyvinyl alcohol which contains, as the sole gelling agent therefor, a gelling amount of from about 1% to about 20% by weight of the amount of weight of polyvinyl alcohol of gelatin, evaporating the resulting dispersion to dryness, and swelling the dried composition thus obtained in cold water, whereby the product is converted to a gel and any water-soluble salts contained therein are washed out.

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3. A method of preparing a light-sensitive photographic emulsion in the form of a thermal-reversible gel, suitable for sensitizing photographic materials and adapted to form a film of tough, transparent colloid having a light-sensitive silver halide dispersed therein, which consists in preparing a dispersion of a light-sensitive silver halide in an aqueous solution of a polyvinyl alcohol which contains, as the sole gelling agent therefor, a gelling amount of from about 1% to about 20% by weight of the amount by weight of polyvinyl alcohol, of bone glue, evaporating the resulting dispersion to dryness, and swelling the dried composition thus obtained in cold water, whereby the product is converted to a gel and any water-soluble salts contained therein are washed out.

4. A method of preparing a light-sensitive photographic emulsion in the form of a thermal-reversible gel, suitable for sensitizing photographic materials and adapted to form a film of tough, transparent colloid having a light-sensitive silver halide dispersed therein, which consists in preparing a dispersion of a light-sensitive silver halide in an aqueous solution of a polyvinyl alcohol which contains, as the sole gelling agent therefor, a gelling amount of from about 1% to about 20% by weight of the amount of weight of polyvinyl alcohol, of glycine, evaporating the resulting dispersion to dryness, and swelling the

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dried composition thus obtained in cold water, whereby the product is converted to a gel and any water-soluble salts contained therein are washed out.

5. A light-sensitive photographic emulsion prepared by the process of claim 1.

6. A light-sensitive photographic emulsion prepared by the process of claim 2.

7. A light-sensitive photographic emulsion prepared by the process of claim 3.

8. A light-sensitive photographic emulsion prepared by the process of claim 4.

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Certificate of Correction

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CARL E. BARNES ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 6, line 70, and column 7, line 28, for the word "of" second occurrence, read *by*; column 6, line 71, after "alcohol" insert a comma;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 13th day of February, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.