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AQUEOUS GELATIN COATING COMPOSITIONS AND THEIR APPLICATION

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This invention relates to gelatin coating solutions particularly for photographic purposes and the employment of those solutions for coating purposes such as in the manufacture of photographic products.

There are numerous instances in industry in which the application of one or more coatings or layers of gelatin is desirable particularly in the making of photographic products. For instance, in the making of photographic paper the application to the paper of a gelatin coating containing pigment such as barium sulfate is conventional. Then there is applied thereover a layer of a photographic emulsion often comprising a suspension of silver halide in an aqueous gelatin solution. Sometimes a layer of aqueous gelatin is applied as an overcoating over the emulsion layer. It is desirable that the coatings be relatively uniform and that the coating operations be carried out at good production speeds.

It is common to utilize coating aids in gelatin coating compositions to facilitate the coating procedure. One of the most common materials which has been employed as a coating aid is saponin. This material has merit in a number of respects but being a naturally occurring material of vegetable origin it may vary in quality and composition from batch to batch; hence uniformity of results may be difficult to procure. It may be in some cases that certain batches of saponin will give an increase in fog, decrease in sensitivity in photographic materials or perhaps cause certain other undesired effects.

Some thought has been given to the use of synthetic materials as coating aids in aqueous gelatin coating compositions. Such synthetic agents because of the controllable nature of their manufacture may be prepared in a uniform manner from one batch to the next both as regards chemical composition and behaviour in use. Several of these synthetic materials have been found useful but there have also been many which have been found to be deficient in one respect or the other. Some coating aids, for instance, which naturally contribute to the ease of coating exhibit adverse photographic properties which limit their use. Some otherwise beneficial synthetic coating aids are inadequate in wet-on-wet type coatings in which a gelatin coating after setting but before drying is overcoated with an aqueous gelatin layer. Various other difficulties may be encountered in the application of gelatin layers to surfaces depending on the coating aid employed.

For a still further appreciation of some of the problems involved in applying gelatin coatings, a brief reference will be made to one method by which such coatings may be applied. One conventional method of applying a gelatin coating to a base involves contacting the base with the coating composition in a simple dip coating technique wherein the material deposited on the base is an amount greater than ordinarily desired in the finished product. The coated base is thereupon passed through

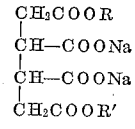
or in the vicinity of some sort of device which levels or otherwise renders such coating more uniform and of the desired thickness. The runback of the excess coating material may cause bubbles in the coating composition in the absence of a suitable coating aid such as is employed in accordance with our invention.

One object of this invention is to provide an improved coating method. An important object is to provide a procedure particularly adapted for the application of gelatin coatings onto cellulosic bases. Another important object of our invention is to provide gelatin coating compositions which can be applied to supports without exhibiting the disadvantages often found in previous gelatin coating operations. Another object of our invention is to provide an improved coating procedure whereby an entire first coating of gelatin may be overcoated by a further gelatin layer with good results. A still further object of our invention is to provide a coating procedure whereby there is a smooth runback of the gelatin coating material from a levelling device. A still further object of our invention is to provide a photographic product comprising a base carrying a relatively uniform and regular gelatin coating thereon which, while containing a coating aid as prescribed by the present invention, possesses excellent photographic properties. Other objects of our invention will appear herein.

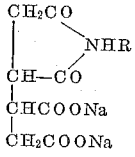
We have found that materials having excellent characteristics for use as coating aids in aqueous gelatin compositions are formed by reacting the dianhydride of tetracarboxy butane with 1 or more equivalents of alcohols or aliphatic amines containing from 8 to 18 carbon atoms followed by treatment of the resulting product with a suitable base such as sodium hydroxide or the like. In general these coating aids may be prepared by treating the dianhydride in a suitable solvent such as dimethyl formamide at an elevated temperature preferably 80–100° C. with the aliphatic alcohol or alkyl amine of at least 1 molar equivalent followed by removal of solvent such as by means of reduced pressure, adding water to the product obtained and treating with a base such as an alkali hydroxide until a pH of about 7 is obtained. The material thus resulting may be added to an aqueous gelatin solution and coated onto a suitable base such as cellulose ester film or sheet. The products obtained ordinarily are mixtures rather than single compounds. Where a molar equivalent of an aliphatic alcohol of 8–18 carbon atoms is employed the product obtained appears to be a mixture of the mono ester, the di-ester and non-esterified tetracarboxy butane (all as the salts). When an aliphatic amine of 8–18 carbon atoms is employed the products obtained appear to be mixtures of the imide and amine salt of the amide. It may be desirable to employ along with the alcohol or amine of 8–18 carbon atoms a lower alcohol or a lower aliphatic amine respectively. In that case some of the substituents in the structure of the resulting compound may be lower alkyl groups. Also in some cases it may be desirable to employ a mixture of an amine and an alcohol in which case an amide ester structure would appear to result.

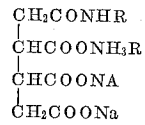
Although ordinarily the base employed for neutralization would be sodium hydroxide, other alkaline materials might be employed for that purpose such as the hydroxides of potassium or lithium or alkali carbonates, ammonia, or amines, such as triethanol amine. Although usually saturated aliphatic alcohols or amines would be employed, the use of unsaturated alcohols or amines such as oleoyl alcohol or an alkenyl amine also comes within the scope of our invention. The product obtained using but a single type of alcohol of 8–18 carbon atoms

and sodium hydroxide as the base would be substantially a compound of the formula:

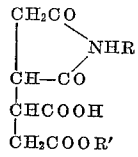


where R is an alkyl or an alkenyl group of 8–18 carbon atoms and $R'=R$ or X in which X is a cation such as Na, Li, K. If different alcohols are employed the radicals represented by R and R' may vary considerably from one molecule to another in any composition derived by the procedure described above. In the case of the reaction of an aliphatic amine of 8–18 carbon atoms followed by treatment with sodium hydroxide the resulting product will comprise a substantial proportion of the following compounds:





In some cases it may be desirable to use both an amine and an alcohol. The resulting product will be principally:



where the alkyl of the alcohol may or may not differ from that of the amine employed. The water-soluble salt of this product will be employed.

The coating aids in accordance with our invention being free of derogatory effects upon gelatin and upon silver halide emusions prepared therefrom may be added to those compositions in any proportion which is sufficient to result in an improvement in the process of applying those compositions either over other layers or supports therefor. We have found, however, that the use of these coating aids in the proportion of 0.13 to 2.0 grams per lb. of the photographic emulsion or of gelatin solution (2–13% concentration) results in satisfactory coating operations. This corresponds to a percentage of 0.03 to 0.45% based on the total weight of the aqueous solution of gelatin.

Photographic emulsions are ordinarily comprised of an aqueous solution of gelatin containing a light sensitive material usually a silver chloride or bromide. The emulsion may contain added materials such as sensitizing dyes, hardeners or other addenda. Descriptions of photographic emulsions are found in the prior art such as in the publication "Fundamentals of Photographic Theory" by James and Higgins, published in 1948 by John Wiley & Sons, chapter 2.

The base to be coated may be composed of any of the conventional film base materials. This may be a sheeting of cellulose ester such as cellulose nitrate or an organic acid ester of cellulose such as cellulose acetate, cellulose acetate propionate or cellulose acetate butyrate. It is often desirable to first apply a subbing layer to the cellulose ester base to contribute to the adhesiveness of the photographic emulsions thereto as is well known in the art. As for paper base, this material before the application of the emulsion is usually coated with a layer of barium sulfate in suspension in a colloid such as gelatin. A description of photographic paper is found in Kodak Data Book, 5th edition, "Kodak Papers," pages 3 and 4. A base material of this type would preferably be employed for preparing photographic paper in accordance with the present invention.

The coating procedure utilized may comprise any of the standard procedures employed in the industry. As an instance of such procedure, the paper base to be coated is passed through a trough or other reservoir whereby a coating is applied to the paper base. The coating is applied in greater thickness than desired and the surface is then subjected to the action of some levelling means such as a doctor blade or an air brush which causes runback of the coating composition and results in an even surface.

We have found that by incorporating products such as are obtained as described herein in a gelatin coating composition that coating of the composition on a support therefor is facilitated and a high quality uniform coating is obtained. In incorporating the coating aid into the aqueous gelatin solution it is usually desirable to add it in the form of dilute aqueous solution. In this manner uniform distribution thereof in the proteinaceous coating composition is obtained.

The following examples illustrate the preparation of products useful as aids in the coating of aqueous gelatin solutions:

Example 1

A mixture of 10 grams (0.05 mole) of tetracarboxybutane-dianhydride in solution in 35 ml. of dimethyl formamide was heated to 70° C. and there was added thereto slowly with stirring 9.3 grams (0.05 mole) of lauryl alcohol. After heating the mass to effect solution of the lauryl alcohol the mixture was heated on the steam bath for one hour. The dimethyl formamide was then removed by vacuum distillation and the syrup resulting was mixed with 150–200 ml. of water and heated to boiling. To the solution was then added aqueous sodium hydroxide solution to bring the pH to 6.7. The resulting solution of approximately 15% strength was useful as a coating aid for incorporation in gelatin coating compositions. The mass was principally the trisodium salt of the mono ester of 1,2,3,4-tetracarboxybutane but might contain small amounts of the salt of the di-ester of 1,2,3,4-tetracarboxybutane and the tetrasodium salt of 1,2,3,4-tetracarboxybutane.

Similar products were prepared from nonyl, undecyl, cetyl, myristyl and oleyl alcohols by substantially the same procedure.

Example 2

28 grams of tetracarboxybutane-dianhydride in solution in 90 ml. of dimethyl formamide was heated to 70° C. and 38 grams of oleyl alcohol was added thereto. This mixture was heated to 100–110° C. for one-half hour and was then cooled to 70° C. and treated with 12 ml. of ethyl alcohol. The mass was heated for a further 2 hours and the dimethyl formamide therein was then removed by distilling under vacuum. A syrup resulted to which 150–200 ml. of water was added and the mass was heated to boiling. Triethanolamine was then added until the pH approached 7. An aqueous solution was obtained which was useful for adding to aqueous gelatin coating compositions. The product obtained was essentially the triethanolamine salt of the ethyl, oleyl ester of tetracarboxybutane. A similar product results when 2 molecular equivalents of oleyl alcohol is employed instead of 1 each of oleyl and ethyl alcohols. Instead of triethanolamine an alkali metal hydroxide may be used for the neutralization step.

Example 3

To a solution of 10 grams of the dianhydride of 1,2,3,4-tetracarboxybutane in 35 ml. of dimethyl formamide heated to 80° C. 9.3 grams of laurylamine was added. The mass was heated for about one-half hour at 90–95° and the dimethyl formamide was removed therefrom by distillation at reduced pressure. The residue was mixed with water and heated and the cloudy mixture resulting was treated with alkali to adjust the pH to approximately

7. A clear solution was obtained which had excellent coating aid properties. Similar coating aid compositions were obtained from decyl, myristyl, cetyl and octadecyl amines.

Example 4

The aqueous solution of the product prepared from 40 grams of 1,2,3,4-tetracarboxybutane dianhydride and 37 grams of laurylamine by the procedure described in the preceding example was evaporated to dryness on the steam bath. Benzene was employed at the end to assist in removing the last traces of water. A pale yellow solid resulted which was redissolved in water to produce solutions of known concentration of excellent coating properties.

The following examples illustrate the use of the coating aids as described herein for gelatin coating compositions.

Example 5

The sodium salt of the laurylamine derivative of tetracarboxybutane such as prepared by the procedure of Example 3 was added to a gelatin-silver halide photographic emulsion in the proportion of 1 gram to 2.5 lb. of emulsion. The emulsion coated readily upon a cellulose ester film base without exhibiting any undesirable properties. This coating aid was incorporated in an aqueous gelatin coating composition of 2% concentration in the proportion of 1 gram of the coating aid per 7.7 lbs. of the coating composition. This composition was applied over the photographic emulsion layer which had been set, but not dried. The ease of applying this overcoating was found to be superior to that observed using other well known coating aids such as saponin.

Example 6

A coating operation involving a coating composition similar to that described in Example 5 was carried out except that the sodium salt of the myristyl amine derivative of tetracarboxybutane was employed as the coating aid in the same concentrations. Similar desirable properties were observed as were obtained in the run in accordance with the preceding example.

Example 7

A gelatin-silver halide photographic emulsion containing the sodium salt of the laurylamine derivative of tetracarboxybutane (prepared by the procedure described in Example 3) in the proportions indicated were coated out onto a baryta coated paper and the following results were obtained:

Grams of coating aid per lb. of emulsion	Repellencies per 7.5/ft.²	Runback at 50 ft./min.
0.0	2	Poor.
.25	0	Good.
.50	2	Good.
1.0	0	Poor.

Example 8

In an experiment similar to that described in the preceding example but using the sodium salt of myristyl amine derivative of tetracarboxybutane as the coating aid the following results were obtained:

Grams of coating aid per lb. of emulsion	Repellencies per 7.5/ft.²	Runback at 50 ft./min.
0.0	2	Poor.
0.13	1	Poor.
.50	0	Good.
1.0	0	Good.

Example 9

In an experiment similar to that described in Example 7 a tetracarboxybutane derivative prepared from a mixture of amines consisting of 90% laurylamine, 9% tetradecyl amine and 1% octadecenyl amine was used in the proportions indicated. The following results were obtained:

Grams of coating aid per lb. of emulsion	Repellencies per 7.5/ft.²	Runback at 50 ft./min.
0.0	6	Poor.
.13	0	Poor.
.25	2	Good.
.5	3	Good.
1.0	0	Good.

Example 10

In an experiment similar to that described in Example 7 the hexadecyl amine derivative was employed with the following results:

Grams of coating aid per lb. of emulsion	Repellencies per 7.5/ft.²	Runback at 50 ft./min.
0.0	4	Poor.
.25	0	Poor.
.5	1	Poor.
1.0	1	Poor.

Example 11

In an experiment similar to that described in Example 7 a decyl amine derivative was employed as the coating aid with the following results:

Grams of coating aid per lb. of emulsion	Repellencies per 7.5/ft.²	Runback at 50 ft./min.
0.0	4	Poor.
.13	1	Poor.
.25	0	Poor.
.5	0	Poor.
1.0	1	Poor.

Example 12

In a similar coating procedure to that of Example 7 the coating aid employed was the monolauryl ester of the trisodium salt of tetracarboxy butane prepared as described in Example 1. The results obtained were as follows:

Grams of coating aid per lb. of emulsion	Repellencies per 7.5/ft.²	Runback at 50 ft./min.
0.0	4	Poor.
0.13	1	Poor.
.25	1	Good.
.5	0	Good.
1.0	0	Good.

The coating aids in accordance with our invention may be employed in admixture with other coating aid materials instead of alone, if desired, such as mixed with oleyl peptides, saponin, oleyl methyl taurine or similar coating aid materials thereby incorporating the advantageous properties of the various coating aids which are added to the gelatin composition.

Esters of tetracarboxybutane with aliphatic alcohols containing from 2 to 10 carbon atoms are excellent plasticizers and solvents for color-forming compounds in light-sensitive silver halide emulsions. In these emulsions the color-forming compound or coupler is dissolved in the tetracarboxybutane ester and dispersed in the gelatino-silver halide emulsion as described in Jelley and Vittum U. S. Patent 2,322,027. The tetraethyl ester as well as the tetra n-propyl, tetra n-butyl, and tetra n-amyl

esters of meso 1,2,3,4-tetracarboxybutane are especially useful for this purpose.

We claim:

1. An aqueous gelatin coating composition comprising an aqueous solution of gelatin of 1½–10% concentration containing therein a small amount of a coating aid selected from the group consisting of the water soluble salts of the esters of aliphatic monohydroxy alcohols of 8–18 carbon atoms and tetracarboxy butane, the water soluble salts of the reaction products which result from heating aliphatic amines of 8–18 carbon atoms with tetracarboxy butane dianhydride and the water soluble salts of the reaction products which result from heating mixtures of aliphatic alcohols and aliphatic amines of 8–18 carbon atoms with tetracarboxy butane dianhydride.

2. An aqueous gelatin coating composition comprising an aqueous solution of gelatin of 1½–10% concentration and as the coating aid therein a small amount of a water soluble salt of an ester of an aliphatic monohydroxy alcohol of 8–18 carbon atoms and tetracarboxy butane.

3. An aqueous gelatin coating composition comprising an aqueous solution of a gelatin of 1½–10% concentration containing as a coating aid therein a small amount of a water soluble salt of the reaction product of an aliphatic amine of 8–18 carbon atoms and tetracarboxy butane.

4. An aqueous gelatin coating composition comprising an aqueous solution of gelatin of 1½–10% concentration containing in dispersion therein a silver halide which solution also contains a small amount of a coating aid selected from the group consisting of the water soluble salts of the esters of aliphatic monohydroxy alcohols of 8–18 carbon atoms and tetracarboxy butane, the water soluble salts of the reaction products which result from heating aliphatic amines of 8–18 carbon atoms with tetracarboxy butane dianhydride and the water soluble salts of the reaction products which result from heating mixtures of aliphatic alcohols and aliphatic amines of 8–18 carbon atoms and tetracarboxy butane dianhydride.

5. In the manufacture of photographic products the steps which comprise incorporating in an aqueous gelatin composition a small amount of a coating aid selected from the group consisting of the water soluble salts of esters of aliphatic monohydroxy alcohols of 8–18 carbon atoms and tetracarboxy butane, the water soluble salts of the reaction products of aliphatic amines of 8–18 carbon atoms and tetracarboxy butane dianhydride and the water soluble salts of reaction products of mixtures of aliphatic alcohols and aliphatic amines of 8–18 carbon atoms and tetracarboxy butane dianhydride and coating out the resulting composition onto a support therefor.

6. In the manufacture of photographic products the steps which comprise incorporating in an aqueous gelatin solution a water soluble salt of an ester of an aliphatic monohydroxy alcohol of 8–18 carbon atoms and tetracarboxy butane and coating out the composition onto a support therefor.

7. In the manufacture of photographic products the steps which comprise incorporating in an aqueous gelatin solution as a coating aid therefor a small amount of a water soluble salt of the reaction product of an aliphatic amine of 8–18 carbon atoms and tetracarboxy butane dianhydride and coating out the composition onto a support therefor.

8. In the manufacture of photographic products the steps which comprise incorporating in an aqueous gelatin composition as a coating aid therefor a small amount of a sodium salt of the lauryl ester of tetracarboxy butane and coating out the composition onto a support therefor.

9. In the manufacture of photographic products the steps which comprise incorporating in an aqueous gelatin composition as a coating aid a small amount of a triethanol amine salt of oleoyl ester of tetracarboxy butane dianhydride and coating out the composition onto a support therefor.

10. In the manufacture of photographic products the steps which comprise incorporating in an aqueous gelatin composition as a coating aid a small proportion of a sodium salt of the reaction product of laurylamine and tetracarboxy butane dianhydride and coating out the composition onto a support therefor.

11. In the manufacture of photographic products the steps which comprise incorporating in an aqueous gelatin composition as a coating aid a small quantity of a sodium salt of the myristoyl amine derivative of tetracarboxy butane and coating out the composition onto a support therefor.

References Cited in the file of this patent

UNITED STATES PATENTS

2,190,645	Boomer	Feb. 20, 1940
2,347,494	Meigs	Apr. 25, 1944
2,606,123	Schmutzler	Aug. 5, 1952
2,666,038	Eisen	Jan. 12, 1954
2,666,700	Baldsiefen	Jan. 19, 1954