United States Patent Office 2,831,766
Patented Apr. 22, 1958

2,831,766

GELATIN COATING COMPOSITIONS

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No Drawing. Application May 17, 1954
Serial No. 430,424

5 Claims. (Cl. 96—94)

This invention relates to gelatin coating compositions adapted for photographic purposes which compositions contain as a coating aid a small proportion of the lauryl or oleyl monoether of polyethylene glycol.

There are many instances in industry where it is desired to apply to a surface one or more coating or layers of gelatin particularly in the making of photographic products. For instance, in the making of photographic paper it is conventional to first apply to the paper a gelatin coating containing barium sulfate or some similar pigment. There may then be applied over this layer a photographic emulsion layer such as of a gelatino silver halide emulsion. Often an overcoating of aqueous gelatin is applied thereover. In commercial operations it is desirable that the coating be relatively uniform and that the coating operations be carried out at good production speeds.

In applying gelatin coatings it has been found desirable to obtain good uniformity of the coatings by incorporating in the gelatin composition a small proportion of a coating aid. Saponin has been useful for that purpose and while it has merit in a number of respects being a naturally occurring material of vegetable origin variation in quality and composition will occur therein from one batch to the next. Hence it is difficult to secure uniformity of results therewith.

Much investigation has been carried out of materials for use as aids in gelatin coating compositions particularly those which can be prepared synthetically. Synthetic agents because of the controllable nature of their manufacture are ordinarily uniformly reproducible from batch to batch as regards both their chemical composition and their behavior. Although a number of synthetic materials have been found to have utility for this purpose, many of these materials have been deficient in that use in one respect or another. For example, some coating aids although facilitating the ease of coating have exhibited adverse photographic properties. Other beneficial synthetic coating aids have been inadequate in wet-on-wet coating where one gelatin coating is overcoated with another gelatin layer after setting but without drying. Various other difficulties have been encountered in the coating of gelatin layers onto a surface depending on the coating aid employed.

For a still further appreciation of some of the problems in the field under consideration a brief reference will be made to a method by which a gelatin coating may be applied. One convenient method of applying gelatin coatings to a base involves contacting the base with the aqueous coating composition in a simple dip coating technique in which the material deposited on the base is in 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 off, or otherwise causes, such coating to be more uniform and of the desired thickness. The run back of the excess coating composition may cause bubbles in the

mass of coating liquid when lacking a coating aid such as is employed in accordance with our invention.

This invention has for one object to provide an improved coating method. An important object is to provide a procedure particularly adapted for the coating of gelatin onto cellulosic bases, such as paper or cellulose ester film base. Another important object is to provide gelatin coating compositions which can be applied to supports therefor without exhibiting the disadvantages which have been found in attempts to coat previous gelatin coating compositions. Another object of our invention is to provide an improved coating procedure whereby an undried first coating of gelatin may be overcoated by further gelatin coating with good results. Still another object of our invention is to provide a coating procedure of the type aforementioned whereby there is smooth run back of the gelatin coating composition from the 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. Other objects will appear herein.

We have found that by the addition of mono-lauryl (dodecyl) or mono-oleyl ethers of polyethylene glycol in certain proportions to gelatin coating compositions the coating properties thereof are enhanced and spotting and formation of bubbles in the coating operation are reduced to a minimum or even eliminated. The compounds which are useful as coating aids in our invention are prepared by heating together a mixture of lauryl or oleyl alcohol and ethylene oxide preferably in an enclosed vessel such as an autoclave as is known in the art. These materials are commercial products. For instance, lauryl ethers of polyethylene glycol are marketed under the name of Brij 35 and mono-oleyl ethers of polyethylene glycol are marketed under the names of Atlas G3920 and Emulphor O. To obtain the desired effect the coating aid should be present in the gelatin solution in free and available form as distinguished from compositions in which those compounds have been employed in preparing suspensions or emulsions which suspensions or emulsions are added to gelatin solutions. The lauryl or oleyl mono ethers of polyethylene glycol which we have found to be the most useful are those having polyethylene chains of 10–25 units per molecule. The aqueous gelatin solutions which are ordinarily employed for photographic coatings have a gelatin concentration of 1½–10%.

In adding the coating aid as prescribed herein the most effective proportions depend upon the particular coating aid employed. For instance in the case of the oleyl ether of polyethylene glycol we have found that the most useful range for use in an aqueous gelatin solution or in a gelatin photographic emulsion is in an amount .01–.5% of the solution or emulsion. Ordinarily the percentages of that coating aid will be selected from the range given. For instance we have found that with some types of gelatin solutions in which the percentage of gelatin is 6–7% the useful range for the addition of this coating aid is 0.14–2.2 grams per lb. of gelatin solution or photographic emulsion (approximately .03–.4%), the preferred range being 0.28 to 1.1 grams per lb. of gelatin solution (approximately .06–.24%).

Where the lauryl ether of polyethylene glycol is employed as the coating aid we have found that the most useful range for use is .0006–.01% of the gelatin solution or emulsion. Proportions of this coating aid in the lower part of the range are particularly effective when used in conjunction with some other appropriate surface active agent such as sodium lauryl sulfate and/or diglycerol mono-laurate. For instance where the lauryl ether of polyethylene glycol has been employed in conjunction with either of these two surface active agents

a suitable range of use for the mixture has been 0.08–0.8 gram per lb. of gelatin photographic emulsion or preferably 0.08–0.2 gram per lb. (approximately .017–.05%), the mono-lauryl ether of polyethylene glycol constituting approximately ⅓ of the amount of surface active agent used. In the case of gelatin coating compositions having a less percentage of gelatin such as 5% thereof or less amounts of the lauryl ether of polyethylene glycol which have been employed in free and available form as low as .036 gram per liter or approximately .0036% have been found to be particularly effective even though no other surface active agent has been employed in conjunction therewith. The amount of free and available coating aid in accordance with our invention which is used is preferably only that which will give the desired coating characteristics to the aqueous gelatin solution or gelatino silver halide emulsion when applied to a support therefore or over other layers which have already been applied thereto.

Photographic emulsions ordinarily comprise a useful solution of gelatin containing a light sensitive material usually a silver salt such as silver chloride, silver chlorobromide or silver bromide. The emulsion may also contain added materials such as sensitizing dyes, hardeners, etc. Descriptions of photographic emulsions are found in the prior art such as in the publication "Fundamentals of Photographic Theory," by James and Higgins, 1948, John Wiley and Sons, chapter 2. Therefore any further detailed description of photographic emulsions here appears to be unnecesary. The coating aids which we employ may be used in both paper emulsions and film emulsions. In the case however of the latter which are ordinarily faster emulsions it is desirable that the coating aids as described herein be used in a proportion no more than is necessary to give good coating properties, to avoid any sensitizing effect from the coating aid which might create a tendency towards fogging in a faster type of emulsion. Ordinarily the amount of the lauryl or oleyl ether used to give a good coating effect will be less than will result in any fogging in the emulsion. Any tendency to impart undesired sensitivity to an emulsion may be corrected by the addition of a suitable antifoggant such as of the type described in application Serial No. 319,614 of Burt H. Carroll, filed November 8, 1952.

The following examples illustrate our invention:

Example 1

A gelatinous silver chlorobromide emulsion was prepared containing 6.5% gelatine and 2.2% silver salts. There was added to this emulsion a mixture of sodium lauryl sulfate, the lauryl mono ether of polyethylene glycol and diglycerol monolaurate, these materials being present in the mixture in the ratio of 3:1:1. The mixture was added in the form of a 2% solution in proportions of 0.08 (.017%), 0.2 (.042%), 0.4 (.08%) and 0.8 (.17%) grams per pound of the emulsion. After thoroughly incorporating the coating aid in the emulsion the resulting composition was coated out onto a baryta coated paper base and the emulsion layer was set, chilled and dried by means of a current of dry air. It was found that there were no repellency spots in the examination of a 7½ sq. ft. area of the paper showing good uniformity in the coating. The photographic quality of the emulsion after this coating aid was incorporated was found to be satisfactory.

Example 2

A gelatinous silver chlorobromide emulsion was prepared containing 8.6% gelatin and 2.9% silver salts. There was added to several portions of the emulsion amounts of coating aid respectively within the range of 0.028–2.2 grams of mono-oleyl ether of polyethylene glycol in the form of its 2% solution. The emulsion was coated onto a baryta coating paper base and dried. It was found that as the amount of coating aid was increased in the gelatin photographic emulsion the number of repellency spots in a 7½ sq. ft. area of their coatings was considerably minimized. It was found that the values from 0.14 to 2.2 grams (.03–.4%) of the coating aid per lb. of the emulsion were the most suitable in this regard.

Example 3

A gelatinous silver chlorobromide emulsion was prepared containing 8.6% gelatin and 2.9% silver salts. There was added to the emulsion mono-oleyl ether of polyethylene glycol in the amount of 0.5 gram per pound of emulsion. The emulsion was coated on a baryta-coated base, chilled and set but was not dried. A coating of a gelatin solution containing 2.5% gelatin and 0.25 gram of the mono-oleyl ether of polyethylene glycol was applied over the set but wet emulsion coat. After setting the overcoat by chilling both coats were dried. It was found that the application of the over-coat was successful and that the elimination of any foam formation in the emulsion composition was possible at speeds somewhat higher than normally used in coating operations.

Example 4

A coating experiment similar to that of the preceding example in which the coating aid employed was replaced by a 1:1 mixture of oleyl ether of polyethylene glycol and N-oleyl N-methyl taurine, sodium salt. The results obtained in the procedure were identical with those reported in Example 3.

The repellency spot test as referred to herein consists in applying an emulsion coating to a support in accordance with the invention described and exposing the emulsion coating to a carbon arc light which "prints out" the emulsion thus darkening the coated area and emphasizing the bare repellency spots. The number of these spots found in a given area of 7½ sq. ft. is determined. To determine the efficacy of the coating aid used the number of spots is compared with the number of such spots obtained when standard coatings are employed. It has been found that by using the coating aids as prescribed herein the number of repellency spots is kept to a minimum. In addition it has been found that the coating aids in accordance with our invention in gelatin coating compositions inhibit the foaming or bubbling which is ordinarily encountered in coating operations employing gelatin emulsions.

Example 5

A gelatino silver halide emulsion to which 0.036 gram of the lauryl mono ether of polyethylene glycol was added per liter of the emulsion was coated out onto a film base and set by chilling but not dried. This emulsion layer was then over-coated with an aqueous solution of gelatin containing .006 gram of sodium lauryl sulfate and .006 gram of the lauryl ether of polyethylene glycol per liter of the gelatin solution which coating was set by chilling and both coatings were then dried in a current of warm dry air. The coatings and both the emulsion and the gelatin overcoat were free from objectionable defects.

The base to be coated by gelatin compositions in accordance with our invention may be composed of any of the conventional film base materials. This may be a sheet of cellulose nitrate or of an organic acid ester of cellulose such as cellulose acetate, cellulose acetate propionate or cellulose acetate butyrate. It is often desirable at first to apply a subbing layer to the cellulose ester base to contribute to the adhesiveness of the photographic emulsion thereto, this subbing practice being well known in the art.

As for photographic paper, a description thereof is found in Kodak Data Book, 5th edition, "Kodak Papers," pages 3 and 4. A base material of the type described there would preferably be employed for preparing photographic paper in accordance with the present invention.

We have found that by incorporating a coating aid of the type described herein in a gelatin coating composition the

coating of that composition on a support therefor is facilitated and a high quality uniform coating is obtained incorporating the coating aid in the form of a dilute aqueous solution such as of 2% concentration and the coating aid is uniformly distributed through the gelatin composition.

The gelatin coating compositions to which coating aid is added in accordance with our invention may be simply aqueous solutions of gelatin per se or they may be gelatin solutions having other materials in suspension or solution therein such as gelatino-silver halide photographic emulsions, barium sulfate-gelatin solutions as used for baryta coating paper base, water soluble dye-gelatin solutions such as may be useful for antihalation coatings, gelatin solutions containing inorganic pigment such as TiO_2, $BaSO_4$, $BaCO_3$, colloidal silica or the like, fibers or other comminuted materials uniformly distributed therein.

We claim:

1. An aqueous gelatin coating composition comprising an aqueous solution of gelatin, 1½–10% concentration, containing a coating aid having the formula:

$$H_3C—O—(CH_2O)_n—R$$

n being within the range of 10–25 and R being a radical selected from oleyl and lauryl, the oleyl compound when selected being 0.01–.5% and the lauryl compound when selected being .0006–.01% of the composition.

2. An aqueous gelatin coating composition comprising an aqueous solution of gelatin, 1½–10% concentration, containing .0006–.01% of a coating aid having the formula:

$$H_3C—O—(CH_2O)_n—(CH_2)_{11}—CH_3$$

n being within the range of 10–25.

3. An aqueous gelatin coating composition comprising an aqueous solution of gelatin, 1½–10% concentration, containing .01–.5% of a coating aid having the formula:

$$H_3C—O—(CH_2O)_n—(CH_2)_8—CH=CH—(CH_2)_7—CH_3$$

n being within the range of 10–25.

4. An aqueous gelatin coating composition comprising an aqueous solution of gelatin of 1½–10% concentration, containing .06–.24% of a coating aid having the formula:

$$H_3C—O—(CH_2O)_n—(CH_2)_8—CH=CH—(CH_2)_7—CH_3$$

n being within the range of 10–25.

5. An aqueous gelatin coating composition comprising an aqueous solution of gelatin of 1½–10% concentration in which silver halide is dispersed, which solution contains a coating aid having the formula:

$$H_3C—O—(CH_2O)_n—R$$

n being within the range of 10–25 and R being a radical selected from oleyl and lauryl, the oleyl compound when selected being 0.01–0.5% and the lauryl compound when selected being .0006–.01% of the composition.

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UNITED STATES PATENT OFFICE

Certificate of Correction

Patent No. 2,831,766 April 22, 1958

William J. Knox et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 22, claim 1, and column 6, line 19, claim 5, the formula in each claim should appear as shown below instead of as in the patent:

$$H—O—(CH_2CH_2O)_n—R$$

column 5, line 31, claim 2, the formula should appear as shown below instead of as in the patent:

$$H—O—(CH_2CH_2O)_n—(CH_2)_{11}—CH_3$$

column 6, lines 4 and 5, claim 3, and lines 11 and 12, claim 4, the formula in each claim should appear as shown below instead of as in the patent:

$$H—O—(CH_2CH_2O)_n—(CH_2)_8—CH=CH—(CH_2)_7—CH_3$$

Signed and sealed this 21st day of April 1959.

[SEAL]

Attest:
KARL H. AXLINE,
Attesting Officer.

ROBERT C. WATSON,
Commissioner of Patents.