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3,091,623

REACTION PRODUCTS OF ISOCYANATO ESTERS AND ALCOHOLS

William J. Knox, Jr., and Charles V. Wilson, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

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3 Claims. (Cl. 260—404.5)

This invention relates to gelatin compositions, coating aids for use therein and the preparation of those aids. This application is a division of our copending application Serial No. 600,679, filed July 30, 1956, now Patent No. 3,038,804.

In the application of gelatin coatings to surfaces and particularly in the photographic industry it is desirable to apply layers of gelatin compositions to surfaces uniformly and at good production speeds. In many cases it is desirable to apply gelatin coatings over previous layers either of gelatin or some other material, the previous layers either being wet or dry.

In the coating of photographic film or paper with a gelatin layer such as of a photographic emulsion or other gelatin compositions an even coating should be obtained. In the absence of a coating aid, numerous crescent shaped uncoated areas may be found in the final product. These defects may be for instance about the size of a pin head with streaks running from the points of the crescent in a direction opposite that of the coating. Often lightly coated areas of 5–10 mm. will appear.

Saponin has been used as the coating aid in gelatin coating compositions, and this use eliminates many of the defects in the coating operations giving a uniformly even coating where the gelatin layer is applied to a dried surface. Saponin, however, may vary markedly from batch to batch both in quality and composition. This material may adversely affect photographic emulsions or even result in no improvement in the coating properties of the composition to which it is added. These variations in quality of the saponin makes the use as a coating aid of a material which is reproducible from batch to batch both in chemical composition and in behavior, desirable. A number of synthetic materials have utility as coating aids in gelatin compositions but they are frequently deficient in one respect or another.

This invention has for an object to provide an improved coating aid for applying aqueous gelatin coatings to either wet or dry surfaces. Another object of our invention is to provide a coating aid for use in photosensitive gelatin emulsions to facilitate the obtaining of coatings which are uniformly even and repellency-free without adversely affecting the emulsion. A further object of our invention is to supply a synthetic chemical compound having valuable characteristics when in aqueous gelatin compositions. A still further object of our invention is to provide a method of preparing compounds useful as coating aids which have the desired properties. Other objects of our invention will appear herein.

We have found that certain novel urethane salts, particularly those prepared in the manner described herein, have valuable properties as coating aids when incorporated in aqueous gelatin compositions which are employed for applying layers to surfaces particularly in photographic applications. These coating aids have been found to impart valuable characteristics to gelatin compositions when incorporated therein in very small quantities such as in amounts of .01% based on the weight of the gelatin. However, larger quantities of these compounds can be used in gelatin compositions to impart good properties

such as in proportions from .01% to 1% or even up to 1% of the dry weight of the gelatin employed in those compositions.

The compounds which have been found to be useful as coating aids are chemically the alkali metal salts of substituted amino acids and can be represented by the following general formula:

$$RX\left[-CONHCH(CH_2)_mCOOM\right]_n \quad (Y)$$

in which R represents a group large enough to bestow surface active properties on the molecule and may be:

(1) A saturated straight or branched chain alkyl group of 8 to 18 carbon atoms,

(2) An unsaturated alkyl group, such as oleyl, linoleyl, linolenyl,

(3) An alkylaryl group in which the alkyl is straight or branched chain and contains 8 to 12 carbons while the aryl group is phenyl.

X=—O—, $—O(CH_2CH_2O)_n—$ in which n=1 to 10, $—CONHCH_2CH_2O—$ or $—CON(CH_2CH_2O)_2=$

Y=H, alkyl group of 1 to 5 carbon atoms, —COOM, or $—CH_2COOM$

m=0, 1, or 2

n=1; or 2 if X is such that two groups can be attached thereto

M=an alkali metal; sodium, potassium or lithium or an ammonium (NH_4) or substituted ammonium radical in which one or more substituents may be a short chain alkyl such as CH_3 or C_2H_5 or hydroxyethyl. The substituents may be the same or different.

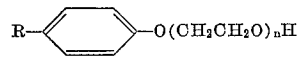
These compounds are most conveniently prepared by a novel procedure in which the alcohol derivative is reacted with an isocyanato ester following which the resulting compound is selectively hydrolyzed with an alkali metal hydroxide, such as sodium hydroxide, to give a water-soluble product which is essentially the sodium salt of a urethane derivative of an amino acid. The isocyanato esters employed may be derived from various amino acids by the procedure of Goldschmidt and Wick (Ann., 575, 217), or by modifications thereof. In essence, this procedure involves treatment of an ester of an amino acid hydrochloride with phosgene at such a rate and at such a temperature that the hydrogen chloride is eliminated from the system, thus yielding the isocyanato ester. Examples of isocyanato esters that may be used in carrying out this reaction are ethyl (or methyl) isocyanatoacetate, methyl or ethyl α-isocyanatopropionate, methyl or ethyl α-isocyanatoisovalerate, dimethyl or diethyl isocyanatosuccinate, dimethyl or diethyl α- or β-isocyanatoglutarate, and dimethyl or diethyl isocyanato malonate. Diisocyanato esters such as those derived from diethyl α,α′-diaminoadipate, or from the esters of leucine are also useful intermediates. The isocyanato esters derived from aspartic and glutamic acids are particularly desirable in forming coating aids in accordance with our invention, but useful products are also obtained with the other isocyanates.

The alcohols which are useful in this reaction include the simple straight or branched chain alcohols containing 8 to 18 carbon atoms, such as lauryl, myristyl, cetyl or octadecyl alcohols or the mixture of coconut oil alcohols; unsaturated alcohols, such as oleyl, linoleyl, linolenyl, and ricinoleyl alcohols; the polyethoxyethanol derivatives of these alcohols of the general formula

$$RO(CH_2CH_2O)_nH$$

in which n is 1 to 10; the polyethoxyethanol derivatives of such alkylarylphenols as p-tert.-octylphenol, nonyl

phenol and dodecylphenol, i.e. products of the general formula



in which R is an alkyl chain of 8 to 12 carbon atoms and n=1 to 10; the hydroxyethyl or hydroxypropyl amides of the general formula

$$RCONH(CH_2)_nOH$$

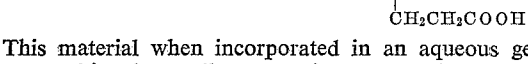
in which R is an alkyl group of 8 to 16 carbon atoms or the oleyl group, and n is 2 or 3; the di-β-hydroxyethyl amides of the general structure

$$RCON(CH_2CH_2OH)_2$$

in which R has the same value as above; the polyethoxyethanol derivatives of the above hydroxyalkyl amides.

In carrying out the reaction an ester is first formed which is selectively hydrolyzed by treatment with one molecular equivalent of alkali for each ester group present. The hydrolysis may be carried out in aqueous or alcoholic solution. The procedure selected usually depends upon the ultimate nature of the product. The sodium salts of the simpler alcohols frequently separate as solid granular materials when the hydrolysis is carried out in a high percentage of alcohol. The polyoxyethanol derivatives usually separate as pastes by this procedure, and it is advantageous in these cases to carry out the hydrolysis in aqueous solution and dilute the product with water to form an aqueous solution of the surface-active agent.

As an example of the process, equimolar amounts of p-tertiary octylphenoxytetraethoxyethanol and dimethyl isocyanatoglutarate yield first an ester and finally the salt of an acid having the following formula:



This material when incorporated in an aqueous gelatin composition in small amount imparts coating properties to that composition which are greatly superior to those of the same composition without a coating aid and are superior to those of similar compositions using saponin as a coating aid.

Although these coating aids can be employed in those compositions in amounts from .01% up to 5% based on the dry weight of the gelatin therein, the amounts employed vary depending upon the coating compositions employed and the conditions of operation. For instance, in the case of photographic emulsions it is desirable to employ a greater proportion of coating aid than in the case of aqueous solutions of gelatin such as are applied as an overcoating. In some compositions where the proportion of gelatin therein is small it migth be desirable to employ amounts of coating aid greater than the minimum specified. Also in the case of high speed coating operations it might be desirable to employ amounts thereof greater than the minimum specified.

Our invention relates to coating onto a base, usually subbed support, gelatin coating compositions, either as aqueous solutions of gelatin or as photographic emulsions which are ordinarily comprised of an aqueous solution of gelatin containing as the light sensitive material a silver salt such as silver chloride, silver bromide, silver iodide or their mixture. The emulsion may contain other added materials such as sensitizing dyes, hardeners or the like. Descriptions of photographic emulsions are found in various places in the prior art, such as in "Fundamentals of Photographic Theory," by James and Higgins; John Wiley and Sons, 1948, chapter 2.

The following examples illustrate the preparation and the use of a representative number of coating aids in accordance with our invention:

Example 1

An X-ray film was prepared in which the photosensitive silver halide emulsion (26 gms. of silver halide and 33 gms. of gelatin per lb. of emulsion) was coated onto a cellulose acetate base and the emulsion layer was overcoated with a gelatin overcoating. There was incorporated in the photographic emulsion 1 gram of disodium N-(carbo-p-tert.-octylphenoxypentaethoxy) aspartate per 2.5 pounds of the emulsion and in the overcoating composition 1 gram of that coating aid was incorporated per 7.7 pounds of aqueous gelatin solution. The overcoating was applied to the emulsion layer on the support while the latter was still wet. In the coating operation the ease of applying the overcoating to the wet photographic emulsion layer was definitely superior to that observed when using saponin. The coating also had the appearance of being very smooth and free of defects or repellencies.

Example 2

A coating operation was repeated as described in Example 1 except that the coating aid employed was disodium N(carbo-p-tert.-octylphenoxypentaethoxy) glutamate. Results of the same nature of those obtained in Example 1 were observed.

Example 3

The coating procedures described in Example 1 were repeated using as the coating aid a disodium N(carbo-p-tert.-octylphenoxypolyethoxy) aspartate in which 7.5 ethylene oxide groups were in the molecule. The coating results obtained were similar to those obtained in the procedure described in the first example.

Example 4

The coating procedure described in Example 1 was duplicated except that disodium N(carbo-p-tert.-octylphenoxypolyethoxy) aspartate containing an average of 9.5 ethylene oxide groups per molecule was used as the coating aid. The results obtained were even superior to those which were obtained in the coatings of Example 1.

Example 5

The procedures of Example 1 were repeated but the coating aid used had an average of 12.5 molecules of ethylene oxide per molecule of coating aid. The results which were obtained substantially corresponded to those which were obtained in the preceding example.

Example 6

An aqueous gelatin coating compositon was prepared in which disodium N(carbo-p-tert.-octylphenoxypentaethoxy) aspartate was used as the coating aid in an amount of 0.25 gram per pound of gelatin coating composition. This composition was coated out onto the back of a photographic film. A coating smooth and free of defects and repellencies was obtained.

In the above examples unless otherwise specified the photographic emulsion compositions contained approximately 36 gms. of gelatin per lb. of wet emulsion and the overcoating compositions approximately 9 gms. of gelatin per lb. of solution. The emulsion was usually applied to the support at the rate of 3.6 lbs. of wet emulsion per 100 sq. ft. of surface and the wet overcoating was usually applied at the rate of 1.6 lbs. of wet overcoat per 100 sq. ft. of surface.

Example 7

A mixture of 22.5 grams of dimethyl isocyanatoglutarate and 1 molar equivalent (47.5 grams) of p-tertiary octylphenoxytetraethoxy ethanol is heated at 80–90° C. for 3 hours. The product which results is dissolved in alcohol and is treated with 2 molar equivalents (9 grams) of sodium hydroxide dissolved in a little water. The mass is heated for one hour at approximately 65° C. resulting in hydrolysis of the product and formation of the sodium salt. The alcohol is driven off and the pasty residue obtained is dissolved in distilled water. A clear aqueous solution of the coating aid is obtained. This

compound exhibits tolerance for calcium and hence can be employed with hard water. When shorter chain alcohols are employed in this reaction such as p-tertiary octylphenoxyethoxy ethanol and p-tertiary octylphenoxydiethoxy ethanol, the sodium salt which is obtained separates as a solid and can be removed from the mass by filtration.

Example 8

Equimolecular quantities of oleyl alcohol and ethyl isocyanato acetate were mixed together. After thoroughly mixing these materials the temperature increased to 80° C. The mass was warmed for an hour at 90–100° C. completing the reaction. The crude urethane thus formed solidified when the mass cooled below 20° C. The crude product was converted by hydrolysis with aqueous alcoholic sodium hydroxide to sodium N-carbo-oleyloxy glycinate. The alcohol was decanted from the pasty mass which was treated with acetone and vigorously stirred. The mass broke up into a granular filter condition. The yield was about 90% of theoretical.

Example 9

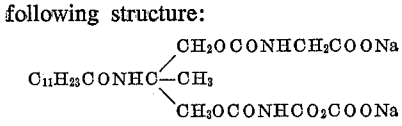
Equimolecular quantities of oleyl alcohol and diethyl alpha isocyanato succinate were mixed and warmed until they had completely reacted. The product obtained was then hydrolyzed by means of two molar equivalents of sodium hydroxide in aqueous alcoholic solution until the sodium salt of the reaction product was obtained. The crude product was agitated in acetone forming a granular material. The product obtained in 90–95% yield was sodium N-carbo-oleyloxy aspartate. This material was found to have valuable properties as a coating assistant.

Example 10

A mixture of equimolecular quantities of N-beta hydroxyethyloleamide and diethyl isocyanatosuccinate was heated for two hours at 100–110° C. The resulting product was dissolved in alcohol and treated with an aqueous solution of 2 molar equivalents of sodium hydroxide. The temperature rose to about 50° C. and the resulting product separated as a paste. Treatment with acetone followed by heating in methyl alcohol and then adding acetone gave a yield of about 88% of an almost white powder which was calcium tolerant and had excellent coating properties. For instance when the product, the sodium salt of N-carbo-β-oleamido ethoxy aspartic acid, was employed in the proportion of 1.25 gms. per lb. of emulsion in the air-knife coating of paper with a gelatino silver halide photographic emulsion at a coating speed of 50 ft. per minute the coating showed improvement over standard coating. In a wet-on-wet coating in which 1 gm. of this coating aid was used in 2.5 lbs. of the photographic emulsion composition and 1 gm. thereof in 7.7 lbs. of the gelatin composition used for overcoating the emulsion layer superior coating properties were exhibited.

Example 11

A mixture of 65 grams of 2-lauroyl amino-2-methyl-1,3-propane diol (obtained by acylating 2-amino-2-methyl-1,3-propane diol with lauroyl chloride in aqueous acetone by the Schotten-Bauman procedure) and 62 grams (about 5% excess) of ethyl isocyanatoacetate was allowed to stand for two hours and was then heated for one hour on the steam bath. About 300 ml. of methanol was added and then a solution of 19.5 grams of sodium hydroxide in 40 ml. of water. After heating for one hour the methanol was removed on the steam bath, ethyl acetate was added and the heating was continued first on the steam bath and then in a vacuum oven. After stirring with acetone the product was collected on a filter. There was obtained 115 grams of a product having the following structure:

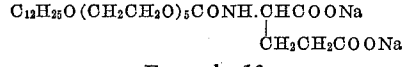


This material is the sodium salt of 3,11-diaza-4,10-dioxo-5,9-dioxa-7-methyl-7-lauroylamino-1,13-tridecanedioic acid.

This product exhibits good coating aid properties both when incorporated in photographic emulsions for coating on paper and in wet-on-wet coating operations in which an emulsion layer is applied to a support and is overcoated with a gelatin coating. For instance this material was incorporated in photographic emulsions in proportions of both 0.5 gm. and 1.0 gm. per lb. of emulsion and good coatings were obtained. This material was incorporated in a photographic emulsion in an amount of 1 gm. per 2.5 lbs. of emulsion and in a gelatin coating composition in the proportion of 1 gm. per 7.7 lbs of composition. The emulsion was applied in the form of a layer to a support and almost immediately thereafter a gelatin overcoating layer was applied thereover. Good results were obtained by this procedure.

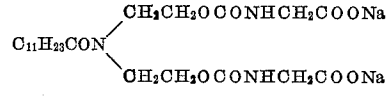
Example 12

A mixture of 80 grams of a product having the structure $C_{12}H_{25}O(CH_2CH_2O)_nH$, in which n averages 5 and 40 grams of dimethyl isocyanato glutarate, was heated at 70–80° C. for about 20 hours. The product obtained was treated with aqueous NaOH composed of 16 grams of caustic in 40 ml. of water. The ester groups were thereby replaced with sodium susbtituents. Upon termination of the reaction, the mass was diluted with water and the hydrolysis procedure was completed by continued heating thereof at about 75° for several hours. The product which is the sodium salt of N-carbo-lauroxy pentaethoxyglutamic acid has a formula represented by the following



Example 13

A mixture was prepared of 60 gms. each of ethyl isocyanatoacetate and di-(betahydroxy ethyl) lauramide. After standing for a time, the temperature rises to approximately 130° C. The mass was protected from atmospheric moisture and was allowed to stand for several hours at 75° C. The resulting product was placed in a vessel and treated carefully with stirring with a mixture of 15 gr. of sodium hydroxide in 40 ml. of water. The mass obtained was diluted with about 100 ml. of water and was heated at 80–90° C. for 5 hours. The mass was then further diluted so as to result in a solution of about 30% solids. The material obtained was essentially the sodium salt of 3,8,13-triaza-4,12-dioxo-5,11-dioxa-8-lauroylpentadecane 1,15-dioic acid. The structural formula of the main ingredient of the product is as follows:



The product can either be dried down to a pale yellow solid or retained in aqueous solution, the material being useful in either case as a coating assistant. For instance gelatino silver halide photographic emulsions containing this product in proportions of 0.25 gm., 0.5 gm. and 1.0 gm. per lb. of emulsion were applied to paper by a hopper coating technique at the rate of 50 ft. per minute. Coatings of good quality were obtained. A wet-on-wet coating experiment was performed using this product in the photographic emulsion at the rate of 1 gm. per 2.5 lbs. of emulsion and in the gelatin overcoating composition at the rate of 1 gm. per 7.7 lbs. of composition. The

photographic emulsion was applied as a layer onto a support and almost immediately thereafter, a layer of the gelatin coating composition was applied thereover. Excellent coating properties were observed.

Example 14

In wet-on-wet coating experiments using X-ray photographic emulsions there was added disodium N-carbo-(para tert. octyl phenoxy pentethoxy) glutamate in proportions of .05, .1 and .5 gm per 2.5 pounds of emulsion and .05, .1 and .5 gm. per 7.7 pounds of overcoating composition. The ease of wet-on-wet overcoating was superior to that obtained when saponin is employed as the coating aid in similar operations. In a similar operation the coating aid used was the sodium salt of N-carbo lauroxy pentethoxy-glutamic acid described in Example 12. The ratio by weight of the coating aid to the emulsion was 1 gm. per 2.5 pounds, and in the overcoating composition 1 gm. of coating aid per 7.7 pounds was used. The ease of wet-on-wet coating with these compositions was decidedly superior to that which is obtained using saponin as a coating aid.

The coating aids described herein are particularly valuable either as the sole coating aid or in admixture with other coating aids for use in coating compositions employed in multiple coating operations such as are described and claimed in application Serial No. 489,863 of Theodore A. Russell, filed February 23, 1955, or in coating operations described in applications Serial Nos. 489,861, 489,862 and 489,969.

The photographic emulsions to which hardeners in accordance with our invention may be added are any of the usual types of photographic emulsions having other additives such as might be useful in imparting certain desirable properties thereto. These emulsions can be chemically sensitized by any of the accepted procedures. For instance, the emulsions can be digested with naturally active gelatin or sensitized sulfur compounds can be added such as those described in Sheppard U.S. Patent Nos. 1,574,944 and 1,623,499 and Sheppard and Brigham, 2,410,689.

The emulsions can also be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium and platinum, all of which belong to group VIII of the periodic table of elements and have an atomic weight greater than 100. Representative compounds are ammonium chloropalladate, potassium chloroplatinate and sodium chloropalladite, which are used for sensitizing in amounts below that which produces any substantial fog inhibition, as described in Smith and Trivelli U.S. Patent 2,448,060, and as antifoggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245 and 2,566,263.

The emulsions can also be chemically sensitized with gold salts as described in Waller and Dodd U.S. Patent 2,399,083 or stabilized with gold salts as described in Damschroder U.S. Patent 2,597,856 and Yutzy and Leermakers U.S. Patent 2,597,915. Suitable compounds are potassium chloroaurite, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole methochloride.

The emulsions can also be chemically sensitized with reducing agents such as stannous salts (Carroll U.S. Patent 2,487,850), polyamines such as diethylene triamine (Lowe and Jones U.S. Patent 2,518,698), polyamines, such as spermine (Lowe and Allen U.S. Patent 2,521,925) or bis-(β-aminoethyl) sulfide and its water-soluble salts (Lowe and Jones U.S. Patent 2,521,926).

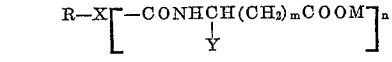
The emulsions can also be stabilized with the mercury compounds of Allen, Byers and Murray U.S. Patent 2,728,663, Carroll and Murray U.S. Patent 2,728,664, and Leubner and Murray U.S. Patent 2,728,665, the tetrazaindenes of Carroll U.S. Patent 2,716,062, and the quaternary benzothiazolium compounds of Brooker and Staud U.S. Patent 2,131,038.

The emulsions may also contain speed-increasing compounds of the quaternary ammonium type of Carroll U.S. Patent 2,271,623, Carroll and Allen U.S. Patent 2,288,226, and Carroll and Spence U.S. Patent 2,334,864, and the polyethylene glycol type of Carroll and Beach U.S. Patent 2,708,162.

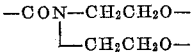
The coating aids of our invention are useful in various kinds of gelatin photographic emulsions. These coating aids are useful not only in nonoptically sensitized emulsions but also in orthochromatic, panchromatic and X-ray emulsions. The coating aid may be added to the emulsion either before or after the addition of any sensitizing dye or sensitizer or other addenda which are incorporated therein. The coating aids of our invention may be employed in gelatin emulsions intended for color photography such as, for example, emulsions containing color-forming couplers or emulsions to be developed by solutions containing color-forming couplers.

We claim:

1. A compound adapted for use as a coating aid having the formula:



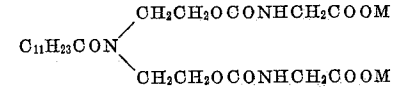
in which m is 0 to 2, n is 1 to 2, R is selected from the group consisting of saturated and unsaturated alkyls and aralkyls, the alkyl radicals thereof being of 8–18 carbon atoms, X is selected from the group of —O—, —$CONHCH_2CH_2O$—,



and —$O(CH_2CH_2O)_n$—, n being 1 to 10, Y is selected from the group consisting of H, the alkyls of 1 to 5 carbon atoms, —CH_2COOM and —CH_2—CH_2COOM and M is selected from the group consisting of Na, K, Li, NH_4, methylamine, ethylamine and hydroxylamine radicals.

2. Disodium N-(carbo-p-tert-octylphenoxy pentaethoxy) glutamate.

3. A compound adapted for use as a coating aid having the formula:



M being an alkali metal substituent.

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2,781,373	Mannheimer	Feb. 12, 1957