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[54] **PHOTOGRAPHIC GELATINOUS COATING COMPOSITION**

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[56] **References Cited**

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[57] **ABSTRACT**

It has been found that photographic gelatinous silver halide emulsions containing dextran sulfate or carboxyalkyl dextran sulfate have increased covering power as well as improved maximum density and contrast.

7 Claims, No Drawings

PHOTOGRAPHIC GELATINOUS COATING COMPOSITION

This invention relates to a photographic gelatinous coating composition which comprises dextran sulfate or carboxyalkyl dextran sulfate.

In the prior art process for the preparation of a gelatinous silver halide photographic emulsion, increased addition of silver halide has been proposed to obtain a higher optical density (or maximum density). However, the highly concentrated amount of silver halide in the photographic emulsion usually causes agglomeration of silver halide particles. Silver particles as reduced after development form so-called "coarse grains," which have remarkably adverse influences on the photographic properties of the resulting silver images. In order to prevent such drawbacks as mentioned above, addition of various additives or adjuvants has been proposed without success.

Recently, an attempt to obtain a higher optical density from a constant amount of reduced silver is made instead of using a higher amount of silver halide. In the preparation of a photographic silver halide emulsion, for example, a natural or synthetic high molecular compound other than gelatine, which compound may be starch etherate, hydroxyethyl cellulose, poly-N-vinyllactam, dextrine, dextran, vinyl-maleic acid copolymer, etc., is added to the photographic emulsion, thereby to obtain increased covering power (the value of the optical density divided by the gram number of developed silver per decimeter square) as well as improved maximum density and contrast. See the specifications of German Pat. No. 1,161,478, U.S. Pat. Nos. 2,495,918 and 3,003,878, British Pat. Nos. 875,100 and 897,497, and Belgian Pat. No. 674,511.

After our extensive studies, it has now been found that photographic gelatinous silver halide emulsions which comprises dextran sulfate or carboxyalkyl dextran sulfate have increased covering power as well as improved maximum density and contrast, while retaining desirable properties owing to gelatine, including sol-gel reversibility depending on temperature change, protective colloidal characteristic for silver halide particles, sensitizing and retarding effects, etc.

The above-mentioned compounds are useful to have about 5–60 percent increase of the covering power of the concerned photographic emulsion. Further they serve to obtain improved maximum density and contrast.

Still another and most important characteristic of these compounds is that they can increase a gellation temperature (i.e. setting point) of the photographic coating composition when it is coated. This is particularly advantageous because it facilitates high speed-coating in the preparation of a photographic material. In the prior art for the manufacture of a light-sensitive photographic material, a photographic light-sensitive gelatinous emulsion, for example, is coated on a support and then blown with cold air thereby to effect setting during the short period of time. Thus, addition of dextran sulfate or carboxyalkyl dextran sulfate to a gelatine-containing photographic coating composition which may be a gelatinous solution for the preparation of an inter layer, protective layer or antihalation layer can increase the setting point of said solution whereby the time required for setting is shortened. In practice, this enables us to simplify the chilling step. For example, it is possible to minimize the required output of a cold air-generating means, e.g. a refrigerator.

Suitable as dextran sulfate and carboxyalkyl dextran sulfate used in this invention are also included their alkali metal salts (i.e. sodium or potassium salt) and alkaline earth metal salts i.e. calcium or magnesium salt) as well as their ammonium salt.

Dextran sulfate and carboxyalkyl dextran sulfate can be prepared from a dextran having an intrinsic viscosity of 0.03–1.7, which is obtained by the partial depolymerization of a native dextran with an acidic or alkaline enzyme, said native dextran being obtained by treating a sugar solution with dextran sucrose separated from the culture solution of a dextran-producing microorganism such as Leuconostoc mesenteroides, Leuconostoc dextranicum, etc. The thus obtained dextran is reacted with a sulfating agent such as chlorosulfonic acid in the presence of a basic organic solvent such as pyridine or formamide, thereby to produce dextran sulfate which is treated with an alkali metal hydroxide, alkaline earth metal hydroxide or oxide or ammonia thereby to obtain the corresponding alkali or alkaline earth metal or ammonium salt of the dextran sulfate. Carboxyalkyl dextran sulfate can be prepared by reacting dextran sulfate with a carboxyalkylating agent such as monochlorocarboxylic acid. Alternatively, dextran is reacted first with a carboxyalkylating agent in alkali medium thereby to produce carboxyalkyl dextran which is then reacted with a sulfating agent in a basic organic solvent to obtain carboxyalkyl dextran sulfate which may be converted into an appropriate salt form.

Dextran has three replaceable hydroxyl groups per anhydrous glucose unit. In theory, therefore, it is possible to effect substitution of up to three hydroxyl groups with sulfate group and/or carboxyalkyl group. By selection of the reaction condition, dextran sulfate and carboxyalkyl dextran sulfate which have any substitution (sulfation and/or carboxyalkylation) degree of up to 3 are obtained. Substitution with a sulfate group may be rated by reference to the sulfur content of dextran sulfate or carboxyalkyl dextran sulfate. For example, the sulfur content of sodium dextran sulfate with a substitution degree of 3 is about 20.5 percent. The starting dextran which is preferred for the purpose of this invention should have an intrinsic viscosity of 0.2–0.6. The product should preferably have a sulfur content of 13–19 percent.

For information, typical examples for the preparation of dextran sulfate and carboxyalkyl dextran sulfate are shown below.

EXAMPLE A

One hundred g. of dextran having an intrinsic viscosity of 0.41 is dissolved in 1,700 ml. The resulting solution is added with 350 ml. of chlorosulfonic acid at 5°–10° C. Then, the mixture is stirred at 25° C. for 10 hours. After completion of the reaction, the said mixture is poured into 6.8 *l* of methanol. The resulting precipitate is recovered by decantation and then dissolved in 1 *l* of water. To the resulting solution, 900 ml. of 40 percent sodium hydroxide is added dropwise.

To the resulting mixture, 5.7 *l* of methanol is poured thereby to cause precipitation. The precipitate formed is collected by decantation and then dissolved in 1 *l* of water. The resulting solution is adjusted at pH 7.5 with hydrochloric acid and then added with 2 *l* of methanol thereby to effect precipitation. The formed precipitate

is collected by filtration and dried under reduced pressure. The product thus obtained is the sodium salt of dextran sulfate with a sulfur content of 16.7 percent.

EXAMPLE B

One hundred g. of dextran having an intrinsic viscosity of 0.54 is dissolved in 1,700 ml. of formamide and the resulting solution is added at 5°–10° C. with 300 ml. of chlorosulfonic acid. The resulting mixture is stirred at 25° C. for 10 hours and thereafter worked up in the same manner as in Example A. The product obtained is the sodium salt of dextran sulfate with a sulfur content of 13.8 percent.

EXAMPLE C

One hundred g. of dextran having an intrinsic viscosity of 0.54 is dissolved in 1,700 ml. of formamide and the resulting solution is added at 5°–10° C. with 30 ml. of chlorosulfonic acid. The resulting mixture is stirred at 25° C. for 10 hours and then poured into 6.8 ml. of methanol. The resulting precipitate is collected by decantation and dissolved in 1 *l* of water. The resulting solution is added dropwise with 90 ml. of 40 percent sodium hydroxide and then added with 3.3 *l* of methanol.

The resulting precipitate is collected by decantation and then dissolved in 1 *l* of water. The resulting solution is adjusted at pH 7.5 with hydrochloric acid and then added with 2 *l* of water. The precipitate formed is collected by filtration and dried under reduced pressure. The product thus obtained is the sodium salt of dextran sulfate with a sulfur content of 4.7 percent.

EXAMPLE D

One hundred g. of dextran having an intrinsic viscosity of 0.039 is dissolved in 1,000 ml. of formamide and the resulting solution is added at 5°–10° C. dropwise with 300 ml. of chlorosulfonic acid. The resulting mixture is stirred at 25° C. for 10 hours and then poured into 4 *l* of methanol to effect precipitation. The resulting precipitate is recovered by decantation.

This precipitate is dissolved in 2 *l* of water and then 250 g. of calcium oxide is added portionwise to the resulted solution. Then, this solution is filtered, and the resulting filtrate is added with 6 *l* of methanol, thereby to form precipitation. The resulted precipitate is dissolved in 1 *l* of water and the resulting solution is adjusted at pH 7.5 with hydrochloric acid and added with 2 *l* of water to cause precipitation. The resulted precipitate is recovered by filtration and then dried under reduced pressure. The product thus obtained is the calcium salt of dextran sulfate with a sulfur content of 19.3 percent.

EXAMPLE E

One hundred g. of dextran having an intrinsic viscosity of 0.039 is dissolved in 1,000 ml. of formamide and added at 5°–10° C. with 300 ml. of chlorosulfonic acid. The resulting mixture is stirred at 25° C. for 10 hours and then it is poured into 4 *l* of methanol. The formed precipitate is recovered by decantation and dissolved in 2 *l* of water. To the resulted solution, 900 ml. of 40 percent sodium hydroxide is added dropwise. To the mixture, 6 of methanol is poured thereby to effect precipitation. The resulted precipitate is recovered by decantation and dissolved in 1 *l* of water. The resulting solution is adjusted at pH 7.5 with hydrochloric acid and then added with 2 *l* of methanol. The formed precipitate is collected by filtration and dried under reduced pressure, thereby to obtain 100 g. of the sodium salt of dextran sulfate which salt is dissolved in 170 ml. of water. To this solution, 43 g. of sodium hydroxide is added. The resulting clear solution is cooled to 5°–10° C. and added with 51.5 g. of monochloracetic acid. After continuing the reaction at 50° C. for 3 hours, the reaction mixture is poured into 450 ml. of methanol to cause precipitation. The resulted precipitate is dissolved in 1 *l* of water and the resulting solution is added with 3 *l* of methanol. The precipitate formed is collected by filtration and dried under reduced pressure. The product thus obtained is the sodium salt of carboxymethyl dextran sulfate, which has an esterification degree of 2.0 and a carboxymethylation degree of 0.1.

EXAMPLE F

One hundred g. of dextran having an intrinsic viscosity of 1.6 is dissolved in 300 ml. of water and then added with 250 g. of sodium hydroxide. The resulting clear solution is cooled to 5°–10° C. and added with 175 g. of monochloracetic acid. After continuing the reaction at 50° C. for 3 hours, the resulting reaction mixture is poured into 600 ml. of methanol to form precipitation. The precipitate thus obtained is dissolved in 1 *l* of water and poured into 3 *l* methanol, thereby to effect reprecipitation. The resulted precipitate is recovered by filtration and dried under reduced pressure to obtain 100 g. of carboxymethyl dextran which is then suspended in 1,000 ml. of formamide. The resulted suspension is added with 20 ml. of concentrated sulfuric acid gradually. The resulting clear solution is added dropwise with 250 ml. of chlorosulfonic acid at 5°–10° C. After continuing the reaction at 50° C. for 3 hours, the resulting reaction mixture is poured into 600 ml. of methanol thereby to form precipitation. The resulting precipitate is dissolved in 1 *l* of water and then added with 3 *l* of methanol to form reprecipitation. The precipitate thus formed is recovered by filtration and dried under reduced pressure thereby to obtain 100 g. of carboxymethyl dextran which in turn is suspended in 1,000 ml. of formamide. The suspension is added with 20 ml. of concentrated sulfuric acid gradually. The resulting clear solution is dropwise added with 250 ml. of chlorosulfonic acid at 5°–10° C. After stirring at 25° C. for 10 hours, the resulting reaction mixture is poured into 4 *l* of methanol. The precipitate formed is recovered by decantation.

The precipitate is dissolved in 1 *l* of water and then poured with 300 ml. of 40 percent sodium hydroxide. To the solution, 5.4 *l* of methanol is poured thereby to form precipitation. The precipitate is recovered by decantation and then redissolved in 1 *l* of water. The resulted solution is adjusted at pH 7.5 with hydrochloric acid and then added with 2 *l* of methanol thereby to form precipitation. The precipitate formed is recovered by filtration and dried under reduced pressure. The product thus obtained is the sodium salt of carboxymethyl dextran sulfate which has an esterification degree of 0.5 and a carboxymethylation degree of 0.2.

The dextran sulfate and carboxyalkyl dextran sulfate can be added in the form of aqueous solution or colloidal dispersion to any photographic gelatinous coating composition. Addition of these compounds to the photographic coating composition which is a gelatinous silver halide emulsion may be made at any stage before,

during or after second ripening. Thus, the photographic emulsion may be ordinary (black-and-white) or color photographic emulsion. It is to be noted that use of the dextran sulfate and carboxyalkyl dextran sulfate according to this invention does not cause any adverse influence on the gold-, sulfur-, optical and chemical sensitization of the concerned emulsion. Further, these compounds can be incorporated jointly with sensitizing dyes, coating aid, hardeners or other photographic additives.

The dextran sulfate and carboxyalkyl dextran sulfate can be satisfactorily used in the amount of 0.2–100 parts by weight per 100 parts by weight of gelatine on dry weight basis. However, this range is not critical and the greater or smaller amount may be used depending on the type and degree of substitution of the dextran sulfate. If the dextran sulfate having unduly lower molecular weight is used in a large amount, uneven coating may occur, and if that having unduly higher molecular weight is used, silver halide particles tend to cause agglomeration. These undesired phenomena can be prevented by controlling the type and amount of the dextran sulfate to be added.

The main purpose of this invention is to obtain the improvement in setting temperatures of photographic coating compositions which may be in the form of emulsions, solutions or dispersions. For this purpose, use of dextran sulfate or carboxyalkyl sulfate according to this invention is very effective, as far as the compositions to be coated contain gelatine. Thus, the present invention is applicable to a wide variety of photographic gelatinous coating compositions including those which are usable for the preparation of a light-sensitive emulsion layer, an inter layer, a sub layer, an antihalation layer, an anti-abrasion layer, a backing layer, etc. It should be noted that the existence of at least one sulfate group in the dextran or carboxyalkyl dextran is quite essential to ensure the improved setting temperature of photographic gelatinous coating composition, since, as is well known, non-sulfated dextran or carboxyalkyl dextran does not show any practical improvement in the setting temperature although these are somewhat effective to improve covering power of reduced silver.

If improved covering power accompanied with improved setting temperature is desired, dextran sulfate or carboxyalkyl dextran sulfate of the invention should be used in a light-sensitive emulsion layer or at least in a layer contiguous therewith.

The following examples describe certain ways in which the principle of the invention has been applied, but are not to be construed as limiting its scope.

EXAMPLE 1

According to a neutral process, a photographic light-sensitive gelatinous silver halide emulsion which comprises 100 g. of moderately active photographic gelatine per 0.35 moles of silver bromoiodide containing 3 mol. percent of silver iodide is prepared. This photographic emulsion is treated by way of gold-sensitization and then subjected to second ripening. The resulted high-speed photographic gelatinous silver halide emulsion is divided to five equal portions, among which one is used as a control sample and the remaining four are individually added with the respective one of the dextran sulfates prepared in Examples A, B, C and D, the dextran sulfates being added as 10 percent aqueous solutions in the amounts indicated below.

The resulting five photographic emulsions are individually coated on cellulose triacetate film bases to give a coating thickness of about 10μ. After drying, each of the resulting film strips are subjected to 1/50 second-exposure according to an intensity scale method using a sensitometer having a color temperature of 5,400° K. The exposed film strips are developed at 20° C. for 5 minutes by using a developer of the following formulation:

N-methyl-p-aminophenol sulfate	1.5 g.
Anhydrous sodium sulfite	25 g.
Hydroquinone	3 g.
Sodium carbonate (monohydrate)	1.5 g.
Potassium bromide	0.5 g.
Water to make up total 1l.	

After treating with a stopper and a fixing solution, the film strips are rinsed with water for 0.5 hour and then dried. Sensitometric tests including measurement of covering power are made with respect to the thus prepared films. The results are set forth in Table 1.

In this table, a photographic speed which is obtained as 0.2 times of the inverse number of the photographic exposure (C.M.S. unit) required for providing a density of 0.2 above fog is expressed as relative value based on the photographic speed of the control sample which is rated as 100. In the measurement of covering power, the silver amount is determined by way of fluorescent X-ray analysis.

TABLE 1

Compound used	Amount of the compound (%)	Photographic Fog	Photographic speed	Gamma	Maximum density	Covering power at 0.7 above fog density
Blank (control sample)	–	0.11	100	1.15	1.49	100
Ex. A	30	0.11	102	1.33	1.92	125
Ex. B	80	0.12	101	1.36	2.01	148
Ex. C	60	0.12	104	1.33	1.99	130
Ex. D	80	0.12	103	1.42	2.22	150

As apparent from the above data, photographic films prepared according to the invention have excellent covering power and are improved in maximum density and contrast.

EXAMPLE 2

Two kinds of sodium dextran sulfates having sulfur contents of 16.2 percent and 13.4 percent are prepared by using varying reaction periods in the method of Example A. These sodium dextran sulfates are added to photographic emulsions prepared by the neutral process as referred to in Example 1. Covering power of these emulsions is measured and the result is set forth in Table 2.

TABLE 2

Compound used	Amount of the compound added to gelatine (%)	Covering power at the density of 0.7
Blank (control sample)	–	100
Sulfur content 16.2%	30	148
Sulfur content 13.4%	30	131

It is apparent that covering power is much more improved by using the greater sulfur content of dextran sulfate if the dextran sulfate has the same intrinsic viscosity.

EXAMPLE 3

A photographic coating solution containing 5 percent gelatine is prepared, said solution being usable for the preparation of an inter layer. Each 100 ml. of the coating solution is added with 0.1 g. of the dextran sulfate of Examples A, B, C and D, respectively. Four coating solutions are thus obtained.

Setting temperatures of these solutions are evaluated by measuring a temperature, according to the PAGI method. In comparison with the setting temperature of a dextran sulfate-free gelatine solutions, the said four solutions show an increase in their setting temperature as set forth in Table 3.

TABLE 3

Compound used	Increase in setting temperature (°C.)
Example A	4.1
Example B	1.8
Example C	1.4
Example D	0.6

The setting temperatures of the photographic coating solutions apparently are increased by addition of dextran sulfate, and the coating operation becomes very easy.

EXAMPLE 4

According to a neutral process, a photographic light-sensitive gelatinous silver halide emulsion which comprises 100 g. of moderately active gelatine per 0.35 moles of silver bromoiodide containing 3 mol. percent of silver iodide is prepared. This photographic emulsion is treated by way of gold-sensitization and then subjected to second ripening. The resulted high-speed photographic gelatinous silver halide emulsion is divided to three equal portions, among which one is used as a control sample and the remaining two are individually added with the respective one of the carboxyalkyl dextran sulfates prepared in Examples E and F, the carboxyalkyl dextran sulfates being added as 10 percent aqueous solutions in this amounts indicated below.

The resulting three photographic emulsions are individually coated on cellulose triacetate film bases to give a coating thickness of about 10μ. After drying, each of the resulted film strips are subjected to 1/50 second-exposure according to an intensity scale method using a sensitometer having a color temperature of 5,400° K. The exposed film strips are developed at 20° C. for 5 minutes by using a developer of the following formulation:

N-methyl-p-aminophenol sulfate	1.5 g.
Anhydrous sodium sulfite	25 g.
Hydroquinone	3 g.
Sodium carbonate (monohydrate)	1.5 g.
Potassium bromide	0.5 g.
Water to make up total 1l.	

After treating with a stopper and a fixing solution, the film strips are rinsed with water for 0.5 hour and then dried. Sensitometric tests including measurement of covering power are made with respect to the thus prepared films. The results are set forth in Table 1.

In this table, a photographic speed which is obtained as 0.2 times of the inverse number of the photographic exposure (C.M.S. unit) required for providing a density of 0.2 above fog is expressed as relative value based on the photographic speed of the control sample which is rated as 100. In the measurement of covering power, the silver amount is determined by way of fluorescent X-ray analysis.

TABLE 4

Compound used	Amount of the compound (%)	Fog	Photographic speed	Gamma	Maximum density	Covering power at 0.7 above fog density
Blank (control sample)	–	0.11	100	1.30	1.50	100
Ex. E	30	0.11	101	1.30	1.55	120
Ex. F	30	0.11	103	1.32	1.59	129

As apparent from the above data, photographic films prepared according to the invention have excellent covering power and are improved in maximum density and contrast.

EXAMPLE 5

Varying amounts of the carboxymethyl dextran sulfate obtained in Example E are added to the photographic emulsions obtained by Example 4. Sensitometric measurements are made in the manner as in Example 4. The results are set forth in Table 5.

TABLE 5

Compound used	Amount of the compound added to gelatine (%)	Fog	Photographic speed	Gamma	Maximum density	Covering power at 0.7 above fog density
Blank	–	0.11	100	1.11	1.39	100
Ex. E	8	0.12	101	1.20	1.50	103
Ex. E	35	0.12	102	1.39	1.64	124
Ex. E	40	0.12	101	1.41	1.75	135

EXAMPLE 6

A photographic coating solution containing 5 percent gelatine is prepared. Each 100 ml. of the coating solution is added with 0.1 g. of the carboxyalkyl dextran sulfate of Examples E and F, respectively. Two coating solutions are thus obtained.

Setting temperatures of these solutions are evaluated by measuring a temperature, according to the PAGI method. In comparison with the setting temperature of carboxyalkyl dextran sulfate-free gelatine solution, the said two solutions show an increase in their setting temperature as set forth in Table 6.

TABLE 6

Compound used	Increase in setting temperature (°C.)
Example E	0.9
Example F	0.9

What is claimed is:

1. A photographic coating composition comprising therein a dextran derivative selected from the group consisting of dextran sulfate and carboxyalkyl dextran sulfate and gelatin.

2. A photographic coating composition as claimed in claim 1, wherein said dextran derivative is present in one or more layers selected from photo-sensitive layer, backing layer, protective layer, anti-halation layer and subbing layer.

3. A light-sensitive photographic silver halide emulsion comprising therein gelatin and a dextran derivative selected from the group consisting of dextran sulfate and carboxyalkyl dextran sulfate.

4. The emulsion as claimed in claim 3, further comprising sulfur-, gold-, reductive or polyalkylene oxide sensitizer.

5. The emulsion as claimed in claim 3, further comprising an optical sensitizer.

6. The emulsion as claimed in claim 3, further comprising a color former.

7. A radiation sensitive, gelatino-silver halide emulsion layer containing a sodium, potassium or ammonium salt of dextran sulfate.

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