

1

3,312,554

PHOTOGRAPHIC ELEMENTS

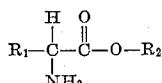
Hans Max Wagner and Thomas Peter Reginald Maynard, Harrow, Middlesex, England, assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey
 No Drawing. Filed Oct. 24, 1963, Ser. No. 318,515
 3 Claims. (Cl. 96-114)

This invention relates to certain polymers which are useful additives for photographic gelatino silver halide emulsions, and to photographic silver halide emulsions containing these polymers.

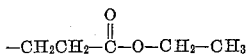
It is well known that certain gelatino silver halide emulsions lose density as the wet-developed layer is dried. It is therefore desirable to provide photographic silver halide emulsions which have a reduced tendency to lose density upon drying.

One object of our invention is to provide certain polymers which are useful additives for photographic gelatino silver halide emulsions. Another object of our invention is to provide photographic silver halide emulsions having a reduced tendency to lose density upon drying and after development. A further object of our invention is to provide photographic emulsions which have increased maximum density. Other objects will appear herein.

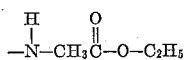
These and other objects of our invention are accomplished by providing polymers which are the reaction product of an ester of an amino acid represented by the following structural formula:



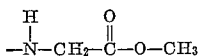
wherein R₁ represents a substituent selected from the group consisting of H; —CH₃;



and —CH₂—CH₂—S—CH₃; and R₂ represents a substituent selected from the group consisting of —CH₃; —CH₂CH₃;



and



with a polymer selected from the group consisting of polyacrylic anhydride, polymethacrylic anhydride, copolymers of alkyl vinyl ether (the alkyl groups of which are from 2-4 carbon atoms) with maleic anhydride, or terpolymers of alkyl vinyl ether (the alkyl group being 2-4 carbon atoms), ethyl acrylate and maleic anhydride.

In one embodiment of our invention we provide copolymers of acrylic acid or methacrylic acid with N-acrylyl (or N-methacrylic) amino acid esters or dipeptide esters, the amino acid esters and dipeptide esters being those described in the above structural formula.

In another embodiment of our invention we provide polymers which are the reaction product of the amino acid and dipeptide esters described above with copolymers

2

of alkyl vinyl ether with maleic anhydride, or terpolymers of alkyl vinyl ether, ethyl acrylate and maleic anhydride.

We have found that when the polymers of our invention are incorporated in gelatino silver halide emulsions, the maximum density of the dried down layer is increased, and that there is a reduction in loss of density on drying.

Our invention will be further illustrated by the following examples.

EXAMPLE 1

Reaction product of polyacrylic anhydride and ethylalanine

Preparation of polyacrylic anhydride: Acrylic anhydride (20 g.) (prepared by the method of Brotherton, Smith and Lynn, J. Org. Chem., 1961, 21, 1283) was dissolved in dry dioxane (200 cc.) in a 250 cc. round bottomed flask. Nitrogen was passed through the solution and azodiisobutyronitrile (0.4 g.) was added. The flask was sealed and placed in a thermostated waterbath at 50° C. for 48 hours when the polymer had completely precipitated. It was collected, washed thoroughly with dry dioxane and dried under vacuum. The yield was 16 g. Reaction with ethylalanine: A solution of polyacrylic anhydride (12.6 g.) in dry dimethylformamide (125 cc.) was added with stirring, while heating on a steambath, to a solution of ethylalanine (16 g.) in dry dimethylformamide (50 cc.). The solution was stirred and heated on the steambath for 18 hours. It was allowed to cool and the polymer was precipitated by pouring the solution into 3 liters anhydrous ether, washed with further portions of ether and dried under vacuum. The yield was 15 g.

The polymer was tested for its ability to reduce loss of density of silver halide emulsions by dissolving in water and adjusting the pH to 6.5. The solution was then added at the rate of 30 grams polymer per mole of silver to a coarse grain bromiodide emulsion which contained 135 g. of gelatin per mole of silver halide. The mixture was then coated onto film support. Strips were cut and exposed for 1/50" in an intensity scale sensitometer, developed for 3 minutes (at 20° C.) in the following developer:

Elon	-----g	2.2
Hydroquinone	-----g	8.8
Anhydrous sodium sulfate	-----g	72.0
Anhydrous sodium carbonate	-----g	48.0
Potassium bromide	-----g	4.0
Water to	-----l	1.0

fixed and washed in the usual manner. Densities were read while the film was wet and after the film had been dried in air at 120° F. and 20% R.H. Characteristic curves were plotted for the wet and dry film and the density differences on drying down were measured at specific densities. Speed was measured as the rel. log (10/E) where E is the exposure required to produce a density of 0.85 above fog. In addition, two slope criteria were calculated: (1) the toe slope—the slope of a line which joins two points on the curve which are at densities of 0.25 and 2.0 above fog; and (2) the shoulder slope—a similar criteria where the points are at densities of 1.0 and 2.5 above fog. Speed, fog and maximum density (dry) were also measured. The results are shown in the following table:

	Rel. Speed	Slope		Fog	D _{max} Dry	Dens. loss at		
		Toe	Shoulder			1.5	2.5	3.5
Control	286	2.56	2.94	.10	3.3	-.13	-.40	-.69
2 Parts polymer Ex. 1 per 9 parts gelatin	292	2.82	3.74	.13	4.3	-.02	-.06	-.20

3 EXAMPLE 2

Reaction product of polyacrylic anhydride and ethyl glycyglycine

The copolymer was prepared by the method described in Example 1 from ethylglycyglycine (8 g.) and polyacrylic anhydride (6.3 g.). There was obtained 8 g. of an almost colorless water soluble powder. The following results were obtained when tested as in Example 1:

	Rel. Speed	Slope		Fog	D _{max} Dry	Dens. loss at		
		Toe	Shoulder			1.5	2.5	3.5
Control.....	286	2.74	3.5	.08	3.60	-.11	-.26	-.46
2 Parts polymer Ex. 2 per 9 parts gelatin.....	290	2.66	4.0	.09	4.0	-.06	-.18	-.24

EXAMPLE 3

Reaction product of polymethacrylic anhydride and ethylglycine

Polymethacrylic anhydride was prepared from methacrylic anhydride by the method described in Example 1 for the preparation of polyacrylic anhydride. This polymer (15.4 g.) in dimethylformamide (250 cc.) solution was reacted with freshly prepared ethylglycine (15 g.) in dimethylformamide (50 cc.) under the conditions of Example 1. A pale cream powder (18 g.) was obtained. On testing, as described in Example 1, the following results were obtained:

	Rel. Speed	Slope		Fog	D _{max} Dry	Dens. loss at		
		Toe	Shoulder			1.5	2.5	3.5
Control.....	286	2.74	3.5	.08	3.60	-.11	-.26	-.46
2 Parts polymer Ex. 3 per 9 parts gelatin.....	291	2.92	4.3	.11	4.0	-.04	Nil	-.12

EXAMPLE 4

Copolymer of methacrylic acid and N-methacrylyl ethylalanine

The copolymer was prepared by the method described in Example 1 from polymethacrylic anhydride (15.4 g.)

added. The jar was closed with a lid containing a rubber seal and placed in a thermostated water bath at 50° C. for 7 days. The solution had become viscous and was precipitated in ether and washed thoroughly in ether. This polymer (15 g.) was then dissolved in dimethylformamide (150 ml.) and added with stirring to a solution of ethylalanine (18 g.) in dimethylformamide (50 ml.). The solution was heated on the steambath for 2½ hours, stirring throughout this period and the polymer was precipitated after cooling, by pouring it into ether. It was washed

with 3 further portions of ether and dried under vacuum. Yield (17 g.).
The polymer was tested as described in Example 1. In the following table are given the results which were obtained.

	Rel. Speed	Slope		Fog	D _{max} Dry	Dens. loss at		
		Toe	Shoulder			1.5	2.5	3.5
Control.....	298	2.66	3.36	.09	3.45	-.14	-.26	-.42
2 Parts polymer Ex. 5 per 9 parts gelatin.....	293	2.70	3.58	.07	3.80	-.04	-.18	-.22

dissolved in dimethylformamide (250 cc.) and ethylalanine (18 g.) dissolved in dimethylformamide (50 cc.). A hygroscopic powder (16 g.) was obtained. The polymer was dissolved in water and added to a coarse grained emulsion as described in Example 1. The following results were obtained:

EXAMPLE 6

Reaction product of copoly(ethyl vinyl ether, maleic anhydride) and ethylglycine

Ethyl vinyl ether, which had been washed with water, dried over solid potassium hydroxide and distilled giving a colorless liquid boiling at 36° C. (40 g.), maleic an-

	Rel. Speed	Slope		Fog	D _{max} Dry	Dens. loss at		
		Toe	Shoulder			1.5	2.5	3.5
Control.....	280	2.74	3.5	.08	3.6	-.11	-.26	-.46
2 Parts polymer Ex. 4 per 9 parts gelatin.....	283	2.98	4.3	.07	4.1	-.08	-.06	-.24

5

hydride (40 g.) and acetone (400 cc.), were placed in a glass pressure jar. Nitrogen was bubbled through the solution and azodiisobutyronitrile catalyst (0.8 g.) was added. The jar was closed with a lid containing a rubber

	Rel. Speed	Slope		Fog	D _{max} Dry	Dens. loss at		
		Toe	Shoulder			1.5	2.5	3.5
Control.....	298	2.54	2.88	.07	3.2	-.20	-.30	-.45
2 Parts polymer Ex. 7 per 9 parts gelatin.....	295	2.88	4.10	.07	3.9	-.08	Nil	Nil

seal and was then placed in a thermostated water bath at 50° C. for five days. The solution had become viscous and was precipitated by pouring it, with rapid stirring, into industrial methylated spirits. After stirring for 15 minutes, the polymer was allowed to settle, the supernatant liquor was decanted and replaced by a fresh portion of methylated spirits (3 l.) and the mixture was stirred for fifteen minutes. The washing process was then repeated.

6

the method described in Example 5. The yield of amino acid derivative was 16.5 g. This polymer was tested as described in Example 1. The following results were obtained.

EXAMPLE 8

Reaction product of polymethacrylic anhydride and ethyl methionine

A copolymer was prepared as described in Example 4 except that ethyl methionine (26.5 g.) was substituted for ethylalanine, and tested as described in Example 1. The following results were obtained:

	Rel. Speed	Slope		Fog	D _{max} Dry	Dens. loss at		
		Toe	Shoulder			1.5	2.5	3.5
Control.....	284	2.62	3.16	.07	3.35	-.12	-.26	-.46
2 Parts polymer Ex. 8 per 9 parts gelatin.....	286	2.82	3.74	.10	4.10	-.06	-.06	-.16

Finally the fibrous, polymeric material was collected and dried in air. Yield (60 g.). This polymer had a viscosity of 6.0 cs. in a 5% solution in acetone.

This polymer (10 g.) was dissolved in dimethylformamide (100 ml.) and the solution was added with stirring to a solution of ethylglycine (9 g.) dissolved in dimethylformamide (30 ml.). The solution was heated, while stirring, on a steambath for 2½ hours and was then allowed

EXAMPLE 9

Reaction product of polyacrylic anhydride and ethyl methionine

The polymer was prepared and tested as described in Example 1 except that ethyl methionine (26.5 g.) was substituted for ethylalanine. The following results were obtained:

	Rel. Speed	Slope		Fog	D _{max} Dry	Dens. loss at		
		Toe	Shoulder			1.5	2.5	3.5
Control.....	284	2.62	3.16	.07	3.35	-.12	-.26	-.46
2 Parts polymer Ex. 9 per 9 parts gelatin.....	284	3.12	4.60	.16	3.80	-.10	Nil	-.14

to cool and precipitated in ether as described in Example 1. (Yield 14 g.). The polymer was tested as in Example 1. The following results were obtained.

	Rel. Speed	Slope		Fog	D _{max} Dry	Dens. loss at		
		Toe	Shoulder			1.5	2.5	3.5
Control.....	298	2.66	3.36	.09	3.45	-.14	-.26	-.42
2 Parts polymer Ex. 6 per 9 parts gelatin.....	296	2.80	3.94	.09	4.00	Nil	-.06	-.04

EXAMPLE 7

Reaction product of terpoly(ethyl vinyl ether, ethyl acrylate, maleic anhydride) and ethylglycine

A terpolymer was prepared as described in Example 5, and 15 g. were then reacted with ethylglycine (14 g.) by

60

EXAMPLE 10

Reaction product of copoly(ethyl vinyl ether-maleic anhydride) and ethyl methionine

The polymer was prepared and tested as described in Example 6 except that ethyl methionine (26.5 g.) was substituted for ethylglycine with the following results:

	Rel. Speed	Slope		Fog	D _{max} Dry	Dens. loss at		
		Toe	Shoulder			1.5	2.5	3.5
Control.....	281	2.54	2.90	.10	3.25	-.13	-.27	-.47
2 Parts polymer Ex. 10 per 9 parts gelatin.....	283	2.80	3.60	.11	3.80	-.11	-.18	-.18

65

EXAMPLE 11

Reaction product of terpoly(ethylvinyl ether-ethylacrylate-maleic anhydride) and ethyl methionine

The polymer was prepared and tested as described in Example 5 except that ethyl methionine (26 g.) was substituted for ethylalanine. The following results were obtained:

	Rel. Speed	Slope		Fog	D _{max} Dry	Dens. loss at		
		Toe	Shoulder			1.5	2.5	3.5
Control.....	281	2.54	2.90	.10	3.25	-.13	-.27	-.47
2 Parts polymer Ex. 11 per 9 parts gelatin....	271	2.64	3.56	.10	3.85	-.16	-.23	-.36

EXAMPLE 12

Reaction product of polymethacrylate anhydride and ethylglutamate

The polymer was prepared and tested as described in Example 4 except that ethylglutamate (28 g.) was substituted for ethylalanine, with the following results:

	Rel. Speed	Slope		Fog	D _{max} Dry	Dens. loss at		
		Toe	Shoulder			1.5	2.5	3.5
Control.....	281	2.6	3.56	.09	3.56	-.24	-.40	-.60
2 Parts polymer Ex. 12 per 9 parts gelatin....	290	2.8	4.20	.10	3.80	-.12	-.24	-.26

The foregoing examples demonstrate that the polymers in accordance with the invention effectively reduce loss of density on drying, and also function to increase the maximum density of gelatino silver halide emulsions. Examples 13 and 14 below demonstrate the unexpected nature of our invention in that certain polymers closely related to those of the invention fail to effectively reduce loss of density upon drying of gelatino silver halide emulsions.

EXAMPLE 13

Reaction product of copoly(methyl vinyl ether-maleic anhydride) and ethylglycine

The above copolymer, having a specific viscosity of 0.1-0.5 was treated with ethylglycine in a manner similar to that described in Example 7 and tested photographically as described in Example 1, with the following results:

	Rel. Speed	Slope		Fog	D _{max} Dry	Dens. loss at		
		Toe	Shoulder			1.5	2.5	3.5
Control.....	290	2.80	3.6	.07	3.58	-.20	-.34	-.60
2 Parts polymer Ex. 13 per 9 parts gelatin....	295	2.76	4.0	.08	4.00	-.20	-.40	-.64

EXAMPLE 14

Reaction product of copoly(ethylene-maleic anhydride) and ethylalanine

The above-identified copolymer was treated with ethylalanine and tested in the manner described in Example 1. The following results were obtained:

	Rel. Speed	Slope		Fog	D _{max} Dry	Dens. loss at		
		Toe	Shoulder			1.5	2.5	3.5
Control.....	287	3.16	3.78	.07	3.76	-.26	-.44	-.62
2 Parts polymer Ex. 14 per 9 parts gelatin....	286	2.96	4.10	.07	3.90	-.16	-.36	-.48

The polymers, copolymers and terpolymers which are reacted with esters of amino acids and dipeptides include polyacrylic anhydride and polymethacrylic anhydride, which are homopolymers. The preferred copolymers of alkyl vinyl ether with maleic anhydride are preferably of the type wherein the two monomeric components alternate in the polymer chain. The exact composition of the terpolymers of alkyl vinyl ether, ethyl acrylate and

maleic anhydride is not known. The moles of the monomeric substituent which are employed in polymerization of these terpolymers may be varied over a wide range, and preferably are about 0.85, 0.625 and 1 moles, respectively, or, in parts by weight, 12.5, 12.5 and 20. The alkyl groups of the alkyl vinyl ether preferably are 2 carbon atoms but may be from 2-4 carbon atoms.

The quantity of amino acid or dipeptide ester reacted with the polymers employed in the invention may vary over a wide range, and advantageously is in excess of one molar proportion of amino acid or dipeptide ester for each anhydride group present, and preferably is from 1.5-2 molar proportions per each anhydride group of the polymer.

The exact chemical nature of the reaction product is not known, but it is believed that under the conditions in which the polymers are made, one of the carboxyl groups liberated on opening the anhydride ring may form a salt. While preliminary analysis points to the formation of a partial amino acid salt, this has not yet been confirmed.

The molecular weight of the copolymers and terpolymers which are reacted with the amino acid and dipeptide esters may vary over a considerable range, and advantageously is such that a 5% solution of the polymer

in acetone at 25° C. has a viscosity of 0.8-2.2 centistokes, and preferably is from 1.3 to 1.8 centistokes.

The polymers of our invention are highly useful, as shown in the foregoing examples, in gelatin silver halide emulsions. The ratio of the polymers of the invention to the gelatin of the emulsion is important, and may vary from 1 to 4 parts by weight polymer to 9 parts by weight

9

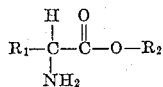
gelatin. The preferred ratio is 1½ to 2¾ by weight polymer to 9 parts by weight gelatin.

Gelatin silver halide emulsions containing the polymer of our invention may be sensitized with any of the well known techniques and additives in emulsion making. The gelatin may contain a plasticizer, such as glycerine, and a gelatin hardener, such as formaldehyde. Other customary photographic emulsion addenda may be present in the emulsion.

This invention has been described in considerable detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

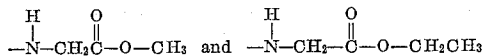
We claim:

1. A photographic silver halide emulsion containing the reaction product of an amino acid ester selected from the group consisting of those represented by the following structural formula:



wherein R₁ represents a substituent selected from the group consisting of H; —CH₃;

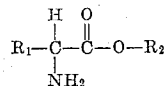
—CH₂CH₂—C(=O)—O—CH₂CH₃;
—CH₂CH₂—S—CH₃; and R₂ represents a substituent selected from the group consisting of —CH₃; —CH₂CH₃;



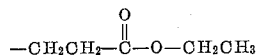
with a polymer selected from the group consisting of polyacrylic anhydride, polymethacrylic anhydride, copolymers of alkyl vinyl ether, the alkyl groups of which contain from 2-4 carbon atoms, with maleic anhydride, and terpolymers of alkyl vinyl ether, the alkyl groups of which contain 2-4 carbon atoms, ethyl acrylate, and maleic anhydride.

10

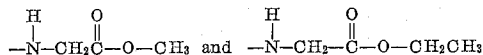
2. A gelatin silver halide emulsion containing the reaction product of an amino acid ester selected from the group consisting of those represented by the following structural formula:



wherein R₁ represents a substituent selected from the group consisting of H; —CH₃;



—CH₂CH₂—S—CH₃; and R₂ represents a substituent selected from the group consisting of —CH₃; —CH₂CH₃;



with a polymer selected from the group consisting of polyacrylic anhydride, polymethacrylic anhydride, copolymers of alkyl vinyl ether, the alkyl groups of which contain from 2-4 carbon atoms, with maleic anhydride, and terpolymers of alkyl vinyl ether, the alkyl groups of which contain 2-4 carbon atoms, ethyl acrylate, and maleic anhydride, the ratio of said reaction product to the gelatin of the emulsion being from 1 to 4 parts by weight reaction product per 9 parts by weight gelatin.

3. A gelatin silver halide emulsion containing, per 9 parts by weight gelatin, 1½ to 2¾ parts by weight of the reaction product of polyacrylic anhydride and ethyl-alanine.

References Cited by the Examiner

UNITED STATES PATENTS

2,409,126 10/1946 Kenyon et al.

NORMAN G. TORCHIN, *Primary Examiner.*

ALEXANDER D. RICCI, *Examiner.*

R. H. SMITH, *Assistant Examiner.*