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3,598,599

POLYMERIC THIAZOLE FOG STABILIZERS FOR PHOTOGRAPHIC EMULSIONS

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19 Claims

ABSTRACT OF THE DISCLOSURE

Polymeric thiazoles containing thiazole groups either incorporated into the polymer chain or appended to the polymer backbone and photographic silver halide emulsions or photographic elements containing fog-stabilizing amounts of such polymeric thiazoles.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to new polymers which are useful as improved antifoggants and stabilizers for photographic elements and to photographic silver halide emulsions containing such polymers as antifoggants and stabilizers therein.

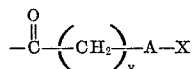
Description of the prior art

During development of a silver halide emulsion, small amounts of silver halide are reduced to metallic silver regardless of whether or not they have been exposed. This reduction of silver ion produces a background fog which is more specifically referred to as chemical fog.

Chemical fog, apparent in most silver halide systems, has been reduced by prior art methods of processing exposed silver halide material in the presence of compounds which restrict development of unexposed silver halide. Such compounds can be incorporated in the silver halide emulsion or in the processing solutions for developing such silver halide emulsions. Compounds which have been found to have a chemical fog inhibiting effect on emulsions which have been subjected to high temperature and high humidity conditions are referred to as emulsion stabilizers. On the other hand, compounds which have been found to have chemical fog inhibiting effects on emulsions which have not been exposed to adverse storage conditions are referred to as antifoggants. Although a large number of emulsion stabilizers and antifoggants have been used in the prior art, many of these compounds cause undesirable losses in emulsion speed and contrast and others lack adequate compatibility with emulsion gelatin.

SUMMARY OF THE INVENTION

According to one embodiment of this invention, there is provided a new class of polymers which are particularly useful as photographic antifoggants and stabilizers. These new polymers contain recurring groups having the formula



wherein y is 0 or 1, the radical —A— is —S— or —NH— and X is a thiazole group. The thiazole groups constitute at least 30% by weight of the polymer and are monovalent when appended to the polymeric backbone and divalent when incorporated into the polymeric backbone.

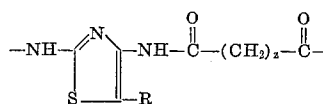
According to another embodiment of this invention, there is incorporated into the silver halide emulsion of a photographic element or in a layer contiguous to the silver halide emulsion, a fog-stabilizing amount of a poly-

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mer containing recurring thiazole groups. The polymer stabilizes the emulsion against fog when the dried emulsion has been subjected to a prolonged high humidity and temperature incubation period without adversely affecting other sensitometric properties. It is an advantage of high molecular weight materials, e.g., polymers, that they remain relatively immobile when incorporated into particular layers of a photographic element.

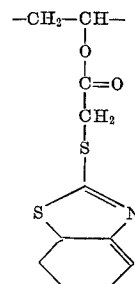
DESCRIPTION OF THE PREFERRED EMBODIMENTS

One preferred group of polymers in accordance with this invention have the thiazole group incorporated into the polymer chain or backbone. These polymers contain repeating segments having the formula

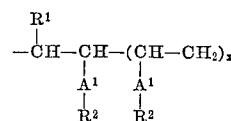


wherein z is an integer of 3 to 8, and R is selected from the group consisting of hydrogen atoms, alkyl (e.g., methyl, ethyl, butyl), and phenyl radicals. Such polymers can be prepared by reacting a diaminothiazole with a dicarboxylic dihalide in an inert solvent.

Another preferred group of polymers have the thiazole groups appended to the polymeric backbone. These polymers contain repeating segments having the formula



or



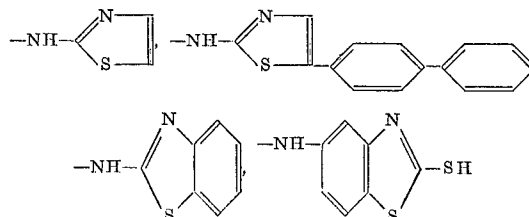
wherein x is 0 or 1, and when x is 0, R^1 is hydrogen, and when x is 1, R^1 is hydrogen or phenyl; A^1 is selected from the group consisting of

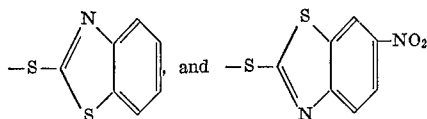


and



radicals; and each R^2 is selected from the group consisting of hydroxy radicals and thioazolyl radicals having the formulae:





at least 25 percent of the total R^2 radicals being said thiazolyl radicals. Such polymers can be prepared by reacting a thiazole which is substituted with a functional group, such as an amino or sulfhydryl group, with a polymer containing reactive groups such as anhydride or ester groups. The reaction can be conducted in the presence of sodium carbonate or sodium hydroxide. When the intermediate polymer is one which contains anhydride groups, such as copoly(styrene-maleic anhydride) or poly(arcylic anhydride), at least half of the A^1R^2 groups in the above formula will be carboxy radicals. Intermediate polymers having intrinsic viscosities of up to about 1.5 are preferred.

The polymeric thiazoles of this invention can be incorporated into a silver halide emulsion of a photographic element or in a layer contiguous to the silver halide emulsion in any amount which will stabilize the silver halide emulsion against fog. In general, a concentration of the polymeric thiazole in an amount of from about 0.10 to about 50.0, preferably about 0.12 to about 19.0 grams per mole of silver in the silver halide emulsion can be used with good results.

The preparation of photographic silver halide emulsions such as are suitably stabilized with a polymeric thiazole typically involves three separate operations: (1) emulsification and digestion of silver halide, (2) the freeing of the emulsion of excess water-soluble salts, suitably by washing with water, and (3) the second digestion or "after-ripening" to obtain increased emulsion speed or sensitivity. (Mees, "The Theory of the Photographic Process," 1954.) The polymeric thiazole can be added to the emulsion before the final digestion or after-ripening or it can be added immediately prior to the coating.

The silver halide emulsion of a photographic element containing the antifoggants of this invention can contain conventional addenda such as gelatin plasticizers, coating aids, and hardeners such as aldehyde hardeners, e.g., formaldehyde, mucochloric acid, glutaraldehyde bis(sodium bisulfite), maleic dialdehyde, aziridines, dioxane derivatives and oxypolysaccharides. Spectral sensitizers which can be used are the cyanines, merocyanines, complex (trinuclear) cyanines, complex (trinuclear) merocyanines, styryls, and hemicyanines. Sensitizing dyes useful in sensitizing such emulsions are described, for example, in U.S. Pats. 2,526,632 of Brooker and White issued Oct. 24, 1950, and 2,503,776 of Sprague issued Apr. 11, 1950. Developing agents can also be incorporated into the silver halide emulsion if desired or can be contained in a contiguous layer. Various silver salts can be used as the sensitive salt such as silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide or silver bromoiodide. The silver halides used can be those which form latent images predominantly on the surface of the silver halide grains or those which form latent images inside the silver halide crystals such as described in U.S. Pat. 2,592,250 of Davey and Knott issued Apr. 8, 1952.

The silver halide emulsion layer of a photographic element containing the antifoggants of the invention can contain any of the hydrophilic, water-permeable binding materials suitable for this purpose. Suitable materials include gelatin, colloidal albumin, polyvinyl compounds, cellulose derivatives, acrylamide polymers, etc. Mixtures of these binding agents can also be used. The binding agents for the emulsion layer of the photographic element can also contain dispersed polymerized vinyl compounds. Such compounds are disclosed, for example, in U.S. Pats. 3,142,568 of Nottorf issued July 28, 1964; 3,193,386 of White issued July 6, 1965; 3,062,674 of Houck, Smith and Yudelson issued Nov. 6, 1962; and

3,220,844 of Houck, Smith and Yudelson issued Nov. 30, 1965; and include the water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

The silver halide emulsion of a photographic element containing the antifoggants of the invention can be coated on a wide variety of supports. Typical supports are cellulose nitrate film, cellulose ester film, polyvinyl acetal film, polystyrene film, poly(ethylene terephthalate) film and related films or resinous materials as well as glass, paper, metal and the like. Supports such as paper which are coated with α -olefin polymers, particularly polymers of α -olefins containing two or more carbon atoms, as exemplified by polyethylene, polypropylene, ethylene-butene copolymers and the like can also be employed.

The speed of the photographic emulsions containing the antifoggants of the invention can be further enhanced by including in the emulsions a variety of hydrophilic colloids such as carboxymethyl protein of the type described in U.S. Pat. 3,011,890 of Gates, Jr., Miller and Koller issued Dec. 5, 1961, and polysaccharides of the type described in Canadian Pat. 635,206 of Koller and Russell issued Jan. 23, 1962.

Photographic emulsions containing the antifoggants of the invention can also contain speed-increasing compounds such as quaternary ammonium compounds, polyethylene glycols or thioethers.

Photographic elements containing the antifoggants of the instant invention can be used in various kinds of photographic systems. In addition to being useful in X-ray and other non-optically sensitized systems, they can also be used in orthochromatic, panchromatic and infrared sensitive systems. The sensitizing addenda can be added to photographic systems before or after any sensitizing dyes which are used.

Silver halide emulsions containing the antifoggants of the invention can be used in color photography, for example, emulsions containing color-forming couplers or emulsions to be developed by solutions containing couplers or other color-generating materials, emulsions of the mixed-packet type such as described in U.S. Pat. 2,698,794 of Godowsky issued Jan. 4, 1955; in silver dye-bleach systems; and emulsions of the mixed-grain type such as described in U.S. Pat. 2,592,243 of Carroll and Hanson issued Apr. 8, 1952.

Silver halide emulsions containing the antifoggants of the invention can be sensitized using any of the well-known techniques in emulsion making, for example, by digesting with naturally active gelatin or various sulfur, selenium, tellurium compounds and/or gold compounds. The emulsions can also be sensitized with salts of noble metals of Group VIII of the Periodic Table which have an atomic weight greater than 100.

Silver halide emulsions containing the antifoggants of the invention can be used in diffusion transfer processes which utilize the undeveloped silver halide in non-image areas of the negative to form a positive by dissolving the undeveloped silver halide and precipitating it on a silver layer in close proximity to the original silver halide emulsion layer. Such processes are described in U.S. Pats. 2,352,014 of Rott issued June 20, 1944; 2,543,181 of Land issued Feb. 27, 1951; and 3,020,155 of Yackel, Yutzy, Foster and Rasch issued Feb. 6, 1962. The emulsions can also be used in diffusion transfer color processes which utilize a diffusion transfer of an imagewise distribution of developer, coupler or dye, from a light-sensitive layer to a second layer, while the two layers are in close proximity to one another. Silver halide emulsions containing the antifoggants of the invention can be processed in stabilization processes such as the ones described in U.S. Pat. 2,614,927 of Broughton and Woodward issued Oct. 21, 1952, and as described in the article "Stabilization Processing of Films and Papers" by H. D. Russell, E. C. Yackel and J. S. Bruce in P.S.A. Journal, Photographic Science and Technique, Volume 16B, October 1950.

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The antifogging agents of this invention can be incorporated to advantage during manufacture in silver halide emulsions representing the variations described above. Moreover, fog control in binderless silver halide films prepared by vapor deposition of silver halide on a suitable support can be achieved by coating the antifogging agents of the invention over the vapor deposited layer of silver halide.

Combinations of all the above-mentioned addenda can be used if desired.

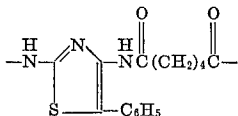
The following examples illustrate the best modes contemplated for carrying out this invention; although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention.

EXAMPLE 1

To a mixture of 2,4-diamino-5-phenylthiazole monohydrobromide (25.5 grams, 0.094 mole) and triethylamine (31 grams, 0.307 mole) in 200 milliliters of dimethylformamide is added in one portion adipyl chloride (17.2 grams, 0.094 mole) with rapid stirring under nitrogen at room temperature. The reaction is allowed to run under ambient conditions for 24 hours. The product is precipitated by pouring the reaction mixture into 2-3 liters of water with stirring. The product is filtered, washed again with water, and dried in a vacuum oven at 40° C. overnight. Yield of light yellow solid is 20.5 grams.

Analysis.—Found (percent): C, 58.0; H, 5.2; N, 14.0; S, 11.8; Cl, 0.5.

The inherent viscosity in dimethylformamide is 0.06. The product consists essentially of repeating segments having the formula

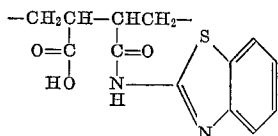


The product is dissolved in dimethylformamide/water (2/1), pH adjusted to 6.3 with 10 percent sodium hydroxide, and subjected to photographic testing as described hereinafter.

EXAMPLE 2

To a solution of copoly(ethylene-maleic anhydride) having an inherent viscosity in dimethylformamide of 0.82 (12.6 grams, 0.1 mole) in 200 milliliters of dimethylformamide is added 2-aminobenzothiazole (15.0 grams, 0.1 mole). The reaction mixture is stirred under nitrogen for 4 hours at 75° C. The entire content is poured into 2-3 liters of diethyl ether with stirring. The supernatant ether is decanted and the precipitate is washed with water and dried in a vacuum oven at 40° C. overnight. The yield of light tan solid is 22.5 grams. After drying, the product is again washed with water, followed by ether and re-dried. The final yield of light tan solid is 16 grams.

Analysis.—Found (percent): C, 54.0; H, 4.8; N, 6.2; S, 6.8. The analytical results for nitrogen and sulfur are consistent with the product containing about 60 percent of the theoretical amount of the benzothiazole system off the polymer chain. The product contains repeating segments having the formula



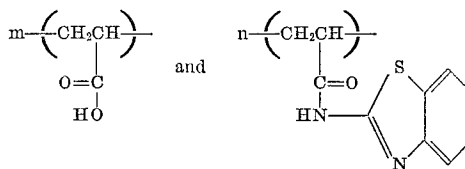
The product is suspended in water and dissolved by adding 10 percent sodium hydroxide. The solution, pH: 6.2, is subjected to photographic testing as hereinafter described.

EXAMPLE 3

The process of Example 2 is repeated substituting for the copoly(ethylene-maleic anhydride) an equimolar

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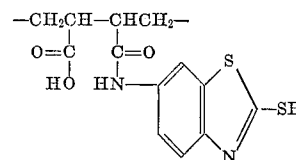
amount of poly(acrylic anhydride) having an inherent viscosity in dimethylformamide of 0.31. The product contains recurring segments having the formulae



wherein the ratio of the values of m to n is about 5:3. Analysis of the product for nitrogen and sulfur indicates that the product contains about 75 percent of the theoretical amount of benzothiazole groups off the polymer chain.

EXAMPLE 4

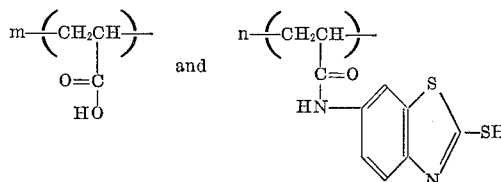
The process of Example 2 is repeated substituting for the 2-aminobenzothiazole an equimolar amount of 2-mercapto-6-aminobenzothiazole and using a copoly(ethylene-maleic anhydride) having an inherent viscosity of 0.13 in dimethylformamide. The product contains repeating segments having the formula



Analysis of the product for nitrogen and sulfur indicates that the product contains about 85 percent of the theoretical amount of 2-mercapto-6-aminobenzothiazole groups off the polymer chain.

EXAMPLE 5

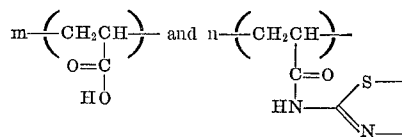
The process of Example 3 is repeated substituting for the 2-aminobenzothiazole an equimolar amount of 2-mercapto-6-aminobenzothiazole and using a poly(acrylic anhydride) having an inherent viscosity in dimethylformamide of 0.79. The product contains recurring segments having the formulae



wherein the ratio of the values of m and n is about 2:1. Analysis of the product for nitrogen and sulfur indicates that the product contains about 70 percent of the theoretical amount of 2-mercapto-6-aminobenzothiazole groups off the polymer chain.

EXAMPLE 6

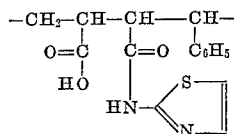
The process of Example 3 is repeated substituting for the 2-aminobenzothiazole an equimolar amount of 2-aminothiazole and using a poly(acrylic anhydride) having an inherent viscosity in dimethylformamide of 0.23. The product contains recurring segments having the formulae



wherein the ratio of the values of m and n is about 4:3. Analysis of the product for nitrogen and sulfur indicates that the product contains about 85 percent of the theoretical amount of 2-aminothiazole groups off the polymer chain.

7 EXAMPLE 7

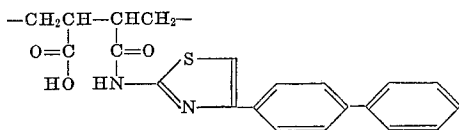
The process of Example 6 is repeated substituting for the poly(acrylic anhydride) an equimolar amount of copoly(styrene-maleic anhydride) having an inherent viscosity in dimethylformamide of 1.37. The product contains repeating segments having the formula



Analysis of the product for nitrogen and sulfur indicates that the product contains about 82 percent of the theoretical amount of the 2-aminothiazole groups off the polymer chain.

EXAMPLE 8

The process of Example 2 is repeated substituting for the 2-aminobenzothiazole an equimolar amount of 2-amino-4-(4-biphenyl)triazole. The product contains repeating segments having the formula



Analysis of the product for nitrogen and sulfur indicates that the product contains about 75 percent of the theoretical amount of 2-amino-4-p-diphenylthiazole groups off the polymer chain.

EXAMPLE 9

Vinyl acetate is polymerized in refluxing methanol solution in the presence of an equimolar amount of chloroform using about 3 percent by weight of monomer of 2,2'-azobis(2-methylpropionitrile) as catalyst. The polymerization is allowed to run for 48 hours at 70° C. under nitrogen. The product is obtained as a tacky, light yellow solid by evaporating off the solvent and washing the residue with ligroine. The product is further purified by dissolving it in a small volume of acetone and precipitating into ligroine. After drying, the yield of tacky solid is about 40–50 percent of the theoretical yield. The inherent viscosity of the product in acetone is 0.13 and the molecular weight is estimated on the basis of chlorine analysis to be between 3000 and 4000. This product is hydrolyzed using sodium hydroxide in methanol to give poly(vinyl alcohol).

Low molecular weight poly(vinyl alcohol) prepared as described above (22 grams, about 0.05 mole) and chloroacetic anhydride (90 grams, 0.525 mole) are heated together in 1000 milliliters of refluxing 1,2-dichloroethane under nitrogen for 4 to 5 hours. The reaction mixture is then poured into 2–3 liters of methanol. The precipitated product is washed with additional methanol and the resulting gummy solid is dried in a vacuum oven overnight. The yield of yellow-tan, flaky solid is 21 grams.

Analysis.—Calcd. (percent): Cl, 29.4. Found (percent): Cl, 26.3.

The calculated chlorine analysis is for the polymer repeating unit without end-groups. The chlorine analysis indicates about 85–90 percent reaction to give the chloroacetate product. Concentration of the mother liquors followed by washing with diethyl ether and reprecipitating from a small amount of acetone with ligroine yielded another 14 grams of gummy product after drying. The product is low molecular weight poly(vinyl chloroacetate).

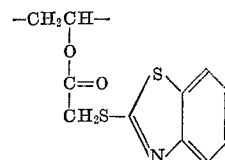
To a solution of poly(vinyl chloroacetate) prepared as described above (12.0 grams, 0.1 mole) in 200 milliliters of dimethylformamide are added 2-mercaptobenzothiazole (16.7 grams, 0.1 mole) and sodium carbonate (5.3 grams, 0.05 mole). The mixture is heated at 70° C.

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for 24 hours under nitrogen with stirring. The reaction mixture is poured into 2–3 liters of water with stirring and filtered. The solid is washed very well with methanol, filtered, and dried in a vacuum oven at 40° C. overnight. The product, 14 grams, is a light tan solid.

Analysis.—Found (percent): C, 52.2; H, 4.5; N, 3.5; S, 18.9; Cl, 5.1.

The analytical results for nitrogen and sulfur are consistent with a product containing about 60–70 percent of the theoretical amount of the benzothiazole system off the polymer chain. The product contains repeating segments having the formula



The product is dissolved in a 1:1 mixture of dimethylformamide and acetone and the solution is subjected to photographic testing as hereinafter described.

EXAMPLE 10

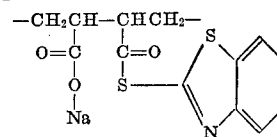
Polyvinyl alcohol having an inherent viscosity in water of 0.4 is treated with chloroacetic anhydride as described in Example 9 to obtain poly(vinyl chloroacetate) having a chlorine content of 28.0%. The product is then reacted with 2-mercaptobenzothiazole as described in Example 9. Analysis of the product for nitrogen and sulfur indicates that the product contains about 82 percent of the theoretical amount of 2-mercaptobenzothiazole groups off the polymer chain.

EXAMPLE 11

2-mercaptobenzothiazole (16.7 grams, 0.1 mole) and sodium hydroxide (4.0 grams, 0.1 mole) are heated in 200 milliliters of dimethylformamide for one hour at 75° C. under nitrogen. Copoly(ethylene-maleic anhydride) having an inherent viscosity in dimethylformamide of 0.13 (12.6 grams, 0.1 mole) is added and the mixture heated at 75° C. for 4 hours under nitrogen. The reaction mixture is poured into 2–3 liters of acetone with stirring. The product is filtered off and dried in a vacuum oven at 40° C. overnight. A purplish solid (15 grams) is obtained. The dry solid is washed very well with methanol and re-dried. Recovery of the product is 13 grams.

Analysis.—Found (percent): C, 39.9; H, 4.4; N, 2.1; 2.6; 2.8; S, <2; Na, 11.6.

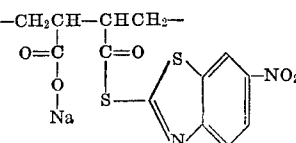
The nitrogen analysis is consistent with a product containing about 50–60 percent of the theoretical amount of the benzothiazole system off the polymer chain. The product contains repeating segments having the formula



The product is dissolved in water and the pH adjusted to 6.4 by the addition of 10 percent aqueous sodium hydroxide. The resulting solution is subjected to photographic testing as described hereinafter.

EXAMPLE 12

The process of Example 11 is repeated substituting for the 2-mercaptobenzothiazole an equimolar amount of 2-mercapto-6-nitrobenzothiazole. The product contains repeating segments having the formula



Analysis of the product for nitrogen and sulfur indicates that the product contains about 25 percent of the theoretical amount of 2-mercapto-6-nitrobenzothiazole groups off the polymer chain.

EXAMPLE 13

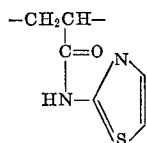
Low molecular weight poly(phenyl acrylate) having a molecular weight of approximately 1060 and terminated with 2-mercaptoethanol (14.6 grams, 0.1 mole) is dissolved in 200 milliliters of distilled N-methylpyrrolidone. 2-aminobenzothiazole (18 grams, 0.18 mole) is added and the reaction mixture is heated with stirring under nitrogen at 160–170° C. for 24 hours. The reaction medium is homogeneous and turns quite dark during the course of the heating period. The product is precipitated by pouring the reaction mixture into 3 liters of distilled water. The precipitate is then washed several times with fresh quantities of water to allow for removal of any unreacted 2-aminobenzothiazole, filtered and dried in a vacuum overnight. The yield of tan solid is about 17 grams.

Analysis.—Found (percent): C, 48.1; H, 5.1; N, 16.6; S, 19.4.

The nitrogen and sulfur analyses are consistent with a product wherein about 90 percent of the phenyl ester groups have reacted to give the thiazolyl-amide linkage.

The product is dissolved in dimethylformamide and tested as an antifoggant as described hereinafter.

The product contains repeating segments having the formula



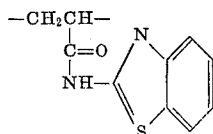
and is terminated at one end thereof by —H and on the other end thereof by the group —SCH₂CH₂OH.

EXAMPLE 14

The process of Example 13 is repeated using poly(phenyl acrylate) having a molecular weight of about 760 terminated with 2-mercaptoethanol and substituting 2-aminobenzothiazole in place of the 2-aminobenzothiazole in about a 1-fold excess. The product is precipitated and washed in methanol rather than in water.

Analysis.—Found (percent): C, 58.3; H, 5.7; N, 12.8; S, 12.4

The nitrogen and sulfur analyses indicate that about 85–95 percent of the phenyl ester groups have reacted to give the benzothiazolyl-amide linkage. The product contains repeating segments having the formula



and is terminated at one end thereof by —H and on the other end by the group —SCH₂CH₂OH.

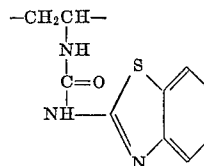
EXAMPLE 15

2-aminobenzothiazole (9.0 grams, 0.06 mole) and vinylisocyanate (4.15 grams, 0.06 mole) are allowed to react in 250 milliliters anhydrous diethyl ether at room temperature under nitrogen for 4–5 hours. Within a few minutes after the reactants are mixed, a white solid begins to separate from the previously homogeneous reaction mixture. At the end of the reaction period, the white precipitate is filtered off, washed with ether and dried. The yield of product, N-vinyl-N'-benzothiazol-2-yl urea, is 11 grams (84 percent).

Analysis.—Calcd. for C₁₀H₉N₃OS (percent): C, 54.8; H, 4.1; N, 19.2; S, 14.6. Found (percent): C, 54.6; H, 3.9; N, 18.8; S, 14.7.

The I.R. and N.M.R. spectra are consistent with the N-vinyl-N'-benzothiazol-2-yl urea structure.

N-vinyl-N'-benzothiazol-2-yl urea is polymerized in refluxing acetone with 1 percent 2,2'-azobis[2-methylpropanitrile] as catalyst for 24 hours under nitrogen. The product precipitates from solution as a white solid during the course of the heating period. The infrared spectrum of the product is consistent with the polymeric structure comprising repeating segments having the formula



The polymer is dissolved in dimethylformamide for testing as an antifoggant.

Each of the compounds prepared in Examples 1 to 15 is added to separate portions of a high speed silver bromide emulsion. For purposes of comparison, high speed silver bromide emulsions are also prepared incorporating the hydrolysis products of the intermediate polymers used in Examples 5 and 11 i.e., polyacrylic acid obtained by hydrolysis of the polyacrylic anhydride having an inherent viscosity in dimethylformamide of 0.79 and copoly(ethylene-maleic acid) obtained by hydrolysis of copoly(ethylene-maleic anhydride) having an inherent viscosity in dimethylformamide of 0.13. Each emulsion sample is coated on a cellulose acetate film support at a coverage of 459 milligrams of silver and 1040 milligrams of gelatin per square foot. A sample of each film coating is exposed on an intensity scale sensitometer, processed for five minutes in Kodak Developer DK-50, fixed, washed and dried. The photographic results obtained from these tests are listed in the table below.

TABLE

Compound of Example	G./mole Ag	Fresh		Incubation at 120° F. and 50% relative humidity for 2 weeks			
		Rel. speed	Gamma	Fog	Rel. speed	Gamma	Fog
Control.....		100	1.28	0.14	26	0.77	0.80
1.....	0.3	65	1.15	0.09	47	0.90	0.21
Control.....		100	1.38	0.11	33	0.80	0.74
2.....	18.4	89	1.52	0.10	60	1.12	0.20
3.....	9.0	97	1.43	0.14	63	1.10	0.29
Control.....		100	1.35	0.17	43	0.80	0.65
4.....	0.45	91	1.35	0.16	67	0.92	0.43
5.....	1.5	80	1.27	0.17	65	1.00	0.29
Control.....		100	1.28	0.14	13	0.48	1.62
6.....	9.0	89	1.27	0.13	60	1.02	0.46
Control.....		100	1.33	0.10	23.5	0.70	0.84
7.....	9.0	64	1.37	0.15	26	0.98	0.31
8.....	9.0	95	1.42	0.13	50	0.97	0.42

TABLE —Continued

Compound of Example	G./mole Ag	Fresh			Incubation at 120° F. and 50% relative humidity for 2 weeks		
		Rel. speed	Gamma	Fog	Rel. speed	Gamma	Fog
Control.....		100	1.25	0.14	110	1.03	¹ 0.33
9.....	9.0	45	0.73	0.10	35	0.68	¹ 0.20
Control.....		100	1.53	0.10	17.2	0.58	1.16
10.....	3.0	87	1.32	0.06	31	0.87	0.74
Control.....		100	1.33	0.10	23.5	0.70	0.84
11.....	9.0	73	1.30	0.10	44	0.95	0.36
Control.....		100	1.28	0.14	53	0.80	0.75
12.....	1.8	85	1.30	0.11	63	0.83	0.49
Control.....		100	1.21	.12	78	1.03	.23
13.....	0.12	76	1.23	.09	80	1.10	.14
Control.....		100	1.36	.27	53	.93	.75
14.....	0.12	85	1.48	.25	69	1.10	.29
Control.....		100	1.50	.15	24	.75	.89
15.....	1.5	102	1.52	.12	27	.83	.81
Control.....		100	1.67	0.16	48	0.95	¹ 0.47
Polyacrylic acid.....	18.0	110	1.65	0.20	35.5	0.85	¹ 0.83
Copoly(ethylene maleic acid).....	45.0	123	1.62	0.24			¹ >1.0

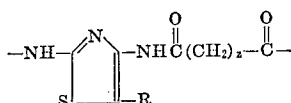
¹ 1-week incubation instead of 2-week incubation.

The results in the above table show that the compounds of the invention prevent the growth of incubation fog when incorporated in photographic emulsions but that polymers which do not contain the thiazole nucleus are either inert or cause fog in photographic emulsions.

Although the invention has been described in considerable detail with reference to certain embodiments thereof, it will be understood that variations and modifications can be effected without departing from the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

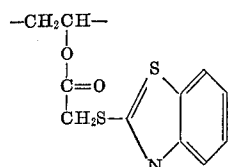
1. A composition comprising a photographic silver halide emulsion stabilized against fog with a fog-stabilizing amount of a polymeric thiazole containing repeating segments having the formula



wherein z is an integer of from 3 to 8 and R is hydrogen, alkyl, or phenyl, wherein the thiazole groups constitute at least 30% by weight of said polymeric thiazole.

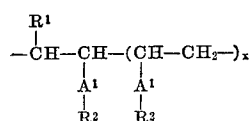
2. The composition of claim 1 wherein said polymeric thiazole is present in an amount of from about 0.12 to about 19.0 grams per mole of silver in said silver halide emulsion.

3. A composition comprising a photographic silver halide emulsion stabilized against fog with a fog-stabilizing amount of a polymeric thiazole containing repeating segments having the formula

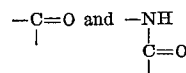


wherein the thiazole groups constitute at least 30% by weight of said polymeric thiazole.

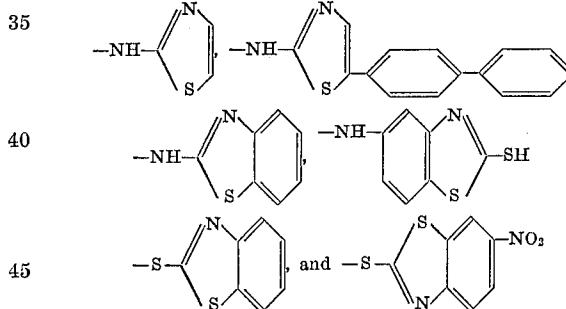
4. A composition comprising a photographic silver halide emulsion stabilized against fog with a fog-stabilizing amount of a polymeric thiazole containing repeating segments having the formula



25 wherein x is 0 or 1, and when x is 0, R^1 is hydrogen, and when x is 1, R^1 is hydrogen or phenyl; A^1 is selected from the group consisting of

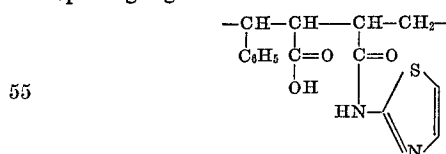


30 radicals; and each R^2 is selected from the group consisting of hydroxy radicals and thiazolyl radicals having the formulae:

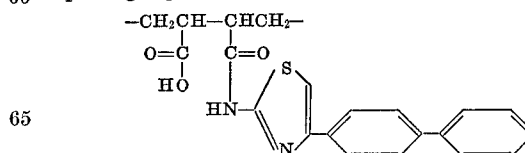


at least 25 percent of the total R^2 radicals being said thiazolyl radicals.

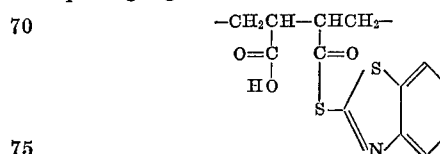
50 5. A composition as set forth in claim 4 wherein said repeating segments have the formula



60 6. A composition as set forth in claim 4 wherein said repeating segments have the formula

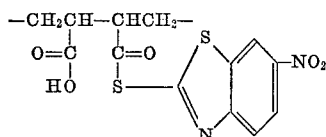


75 7. A composition as set forth in claim 4 wherein said repeating segments have the formula

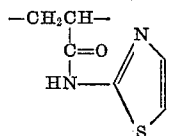


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8. A composition as set forth in claim 4 wherein said repeating segments have the formula

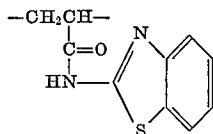


9. A composition as set forth in claim 4 wherein said repeating segments have the formula



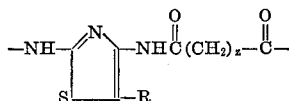
and wherein the polymer is terminated on one end thereof by ---H and on the other end thereof by the group $\text{---SCH}_2\text{CH}_2\text{OH}$.

10. A composition as set forth in claim 4 wherein said repeating segments have the formula



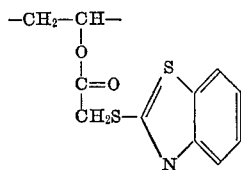
and wherein the polymer is terminated on one end thereof by ---H and on the other end thereof by the group $\text{---SCH}_2\text{CH}_2\text{OH}$.

11. A photographic element comprising a support coated with a silver halide layer, said element stabilized against fog by a fog-stabilizing amount of a polymeric thiazole containing repeating segments having the formula



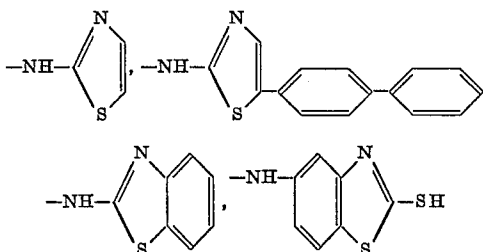
wherein z is an integer of from 3 to 8, and R is hydrogen, alkyl, or phenyl, and wherein the thiazole groups constitute at least 30% by weight of said polymeric thiazole.

12. A photographic element comprising a support coated with a silver halide layer, said element stabilized against fog by a fog-stabilizing amount of a polymeric thiazole containing repeating segments having the formula

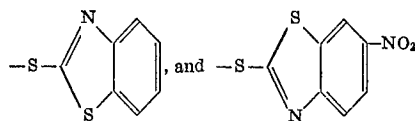


wherein the thiazole groups constitute at least 30% by weight of said polymeric thiazole.

13. A photographic element comprising a support coated with a silver halide emulsion, said element stabilized against fog by a fog-stabilizing amount of a polymeric thiazole containing repeating segments having the formulae

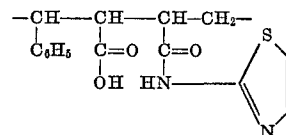


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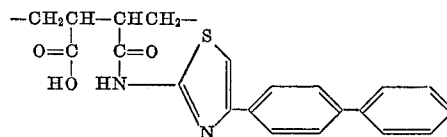


at least 25 percent of the total R^2 radicals being said thiazolyl radicals.

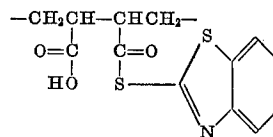
14. A photographic element as set forth in claim 13, wherein said repeating segments have the formula



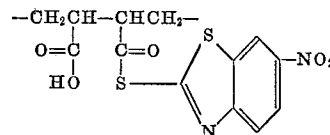
15. A photographic element as set forth in claim 13, wherein said repeating segments have the formula



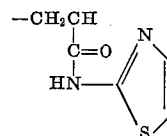
16. A photographic element as set forth in claim 13, wherein said repeating segments have the formula



17. A photographic element as set forth in claim 13, wherein said repeating segments have the formula

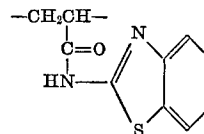


18. A photographic element as set forth in claim 13, wherein said repeating segments have the formula



and wherein the polymer is terminated on one end thereof by ---H and on the other end thereof by the group $\text{---SCH}_2\text{CH}_2\text{OH}$.

19. A photographic element as set forth in claim 13, wherein said repeating segments have the formula



and wherein the polymer is terminated on one end thereof by ---H and on the other end thereof by the group $\text{---SCH}_2\text{CH}_2\text{OH}$.

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U.S. Cl. X.R.

96-114