

- [54] **HARDENABLE VEHICLES FOR SILVER HALIDE EMULSIONS**
 [75] Inventors: **Ignazio Salvatore Ponticello; Ernest John Perry**, both of Rochester, N.Y.

[73] Assignee: **Eastman Kodak Company**, Rochester, N.Y.

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Related U.S. Application Data

[63] Continuation of Ser. No. 394,002, Sept. 4, 1973, abandoned.

[52] U.S. Cl. **96/114**
 [51] Int. Cl.² **G03C 1/72**
 [58] Field of Search **96/114**

[56] References Cited

UNITED STATES PATENTS

3,459,790	8/1969	Smith.....	96/114
3,488,708	11/1970	Smith.....	96/114
3,554,987	1/1971	Smith.....	96/114
3,632,341	1/1972	Salesin et al.....	96/114
3,775,129	11/1973	Dodwell.....	96/114
3,799,781	3/1974	Fitzgerald et al.....	96/114
3,811,897	5/1974	Babbitt et al.....	96/114

FOREIGN PATENTS OR APPLICATIONS

45-2726 1970 Japan..... 96/114

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Dow Corning "Silicon Notes" Bulletin 05-014 June, 1962.
 Mazarov et al., Zh. Obshch Khim, 23 pp. 1793-1801 (1953).

Wenhert et al., J. Am. Chem. Soc. Vol. 86, pp. 2038-2043 (1964).

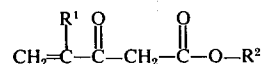
Stork et al., Tetrahedron Letters Vol. 27 pp. 2755-2758 (1972).

Primary Examiner—Jack P. Brammer
Attorney, Agent, or Firm—A. H. Rosenstein

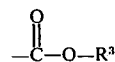
[57] ABSTRACT

A photographic element comprising a support having coated thereon at least one photographic silver halide emulsion and at least one binding agent comprising a film-forming, addition interpolymers comprising

A. from about 1 to about 50% by weight of a polymerized monomer containing active methylene groups and having the formula



wherein R¹ is hydrogen, methyl or



and R² and R³ are independently selected from the group consisting of alkyl radicals, cycloalkyl radicals and aryl radicals; and

B. from about 50 to about 99% by weight of at least one additional polymerized ethylenically unsaturated monomer free of active methylene groups.

18 Claims, No Drawings

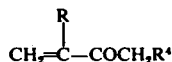
HARDENABLE VEHICLES FOR SILVER HALIDE EMULSIONS

This is a continuation of application Ser. No. 394,002, filed Sept. 4, 1973, now abandoned.

This invention relates to organic materials which are particularly useful in the photographic field. In one of its aspects, this invention relates to the preparation and use of such organic materials, particularly polymeric materials which can be incorporated into photographic elements and emulsions to obtain a desirable combination of properties.

Photographic elements employed in photography, particularly in the graphic arts industry for the production of lithographic plates, must have good physical and photographic properties. Due to its unique properties, including its good dispersing property and its excellent protective colloid properties, gelatin has been used as the binding agent in layers of photographic elements for many years. Gelatin is, however, subject to dimensional change when subjected to varying temperature, humidity and like conditions. Many natural and synthetic materials have been proposed as substitutes for gelatin in one or more layers of photographic elements to improve dimensional stability. For example, as shown in U.S. Pat. No. 3,062,674 issued Nov. 6, 1962 and U.S. Pat. No. 3,142,568 issued July 28, 1964, vinyl or addition polymers are employed in binding agents in layers of photographic elements to improve physical properties, including dimensional stability. However, the use of such polymers in layers of photographic elements, often adversely affects the hardness of the layers, their resistance to abrasion, and their adhesion to film supports.

Japanese Pat. No. 7,002,726 describes a copolymer of the general formula



where R and R⁴ are hydrogen or a lower alkyl, halide, OH, or acetyl or acetoxyl group and at least one vinyl monomer selected from styrene, acrylonitrile, vinyl acetate, vinyl chloride, ethyl methacrylate and acrylamide.

Polymers containing active methylene groups which serve as crosslinking sites that are reactive with conventional gelatin hardeners are disclosed in U.S. Pat. Nos. 3,459,790; 3,488,708; 3,554,987 and 3,658,878. In these polymers, the active methylene group is located in a side chain and is linked to the main chain of the polymer through an ester group. Use of these polymers has, in large measure, resolved the problem of adverse effects upon layer hardness, resistance to abrasion and adhesion to film supports referred to above. Under certain conditions, however, this ester group may tend to hydrolyze with consequent loss of the crosslinking site. It is evident, therefore, that a substitute for gelatin which is not subject to such defects will greatly enhance the art.

Accordingly, it is an object of this invention to provide crosslinkable polymers containing active methylene crosslinking sites in a proportion of the side chains, wherein the group joining the side chain to the polymer backbone possesses increased resistance to hydrolysis.

It is another object of this invention to provide such improved polymers for use, either alone or in admixture with gelatin, as binding agents for photographic layers such as photographic emulsions.

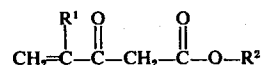
It is a further object of this invention to provide polymers having the desirable properties described above that can be hardened, with conventional gelatin hardening agents, for example, aldehydes and bis(vinylsulfonyl) compounds.

Still another object of this invention is to provide procedures for preparing such hardenable polymers.

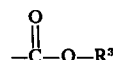
Other objects of this invention will become apparent from an examination of the specification and Claims which follows.

In accordance with this invention, it has been found that an ethylenically-unsaturated monomer containing an active methylene function linked to the unsaturated portion of the monomer by a carbonyl group can be polymerized with at least one additional monomer free of the active methylene function to yield polymers which are useful as gelatin extenders and modifiers which will crosslink with the common gelatin hardening agents. More particularly, the present invention comprises a photographic element comprising a support having coated thereon at least one photographic silver halide emulsion and at least one binding agent comprising a film-forming, addition interpolymer comprising

A. from about 1 to about 50% by weight of a polymerized monomer containing active methylene groups and having the formula



wherein R¹ is hydrogen, methyl or

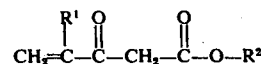


and R² and R³ are independently selected from the group consisting of alkyl radicals, cycloalkyl radicals and aryl radicals; and

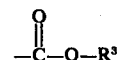
B. from about 50 to about 99% by weight of at least one additional polymerized ethylenically unsaturated monomer free of active methylene groups.

In another aspect, the present invention comprises a photographic silver halide emulsion containing a binding agent comprising a film-forming, addition interpolymer comprising

A. from about 1 to about 50% by weight of a polymerized monomer containing active methylene groups and having the formula



wherein R¹ is hydrogen, methyl or



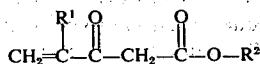
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and R^2 and R^3 are independently selected from the group consisting of alkyl radicals, cycloalkyl radicals and aryl radicals; and

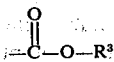
B. from about 50 to about 99% by weight of at least one additional polymerized ethylenically unsaturated monomer free of active methylene groups.

In still another and preferred aspect, the present invention comprises a photographic element comprising a support having deposited thereon at least one photographic silver halide emulsion containing a binding agent comprising a film-forming, addition interpolymer comprising

A. from about 1 to about 50% by weight of a polymerized monomer containing active methylene groups and having the formula



wherein R^1 is hydrogen, methyl or



and R^2 and R^3 are independently selected from the group consisting of alkyl radicals, cycloalkyl radicals and aryl radicals; and

B. from about 50 to about 99% by weight of at least one additional polymerized ethylenically unsaturated monomer free of active methylene groups.

The monomers of this invention containing the active methylene groups are reacted with at least one other ethylenically unsaturated monomer free of active methylene groups to form a polymeric substance. The polymers employed in photographic materials according to the practice of this invention are addition interpolymers containing active methylene groups in the side chains of the interpolymers. Active methylene groups are methylene groups between two activating groups, for example, electronegative groups such as carbonyl. Such methylene groups exhibit unusual chemical activity and are said to be "active".

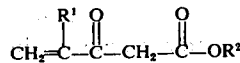
The molecular weights of the polymers employed in photographic emulsions and elements according to the practice of this invention are subject to wide variation, but are often in the range of about 5000 to about 500,000. These polymers, which are generally water soluble, have inherent viscosities (0.25 g. polymer in 100 ml. 1 N. sodium chloride at 25°C.) from 0.7 to 2.0, preferably from about 0.9 to about 1.25.

As noted above, at least about 50% by weight of the polymers of this invention comprises at least one additional polymerized ethylenically unsaturated monomer free of active methylene groups. As exemplary of such monomers may be listed: vinyl esters, amides, nitriles, ketones, halides, ethers, alpha,beta unsaturated acids or esters thereof, olefins, diolefins and the like, as exemplified by acrylonitrile, methacrylonitrile, styrene, alpha-methyl styrene, acrylamide, vinyl chloride, methyl vinyl ketone, fumaric, maleic and itaconic esters, 2-chloroethylvinyl ether, acrylic acid, sodium methacryloyloxyethyl sulfate, methacrylic acid, dimethylaminoethyl methacrylate, 4,4'-9-trimethyl-8-oxo-7-oxa-4-azonia-9-decene-1-sulfonate, N-vinylsuccinamide, N-vinylphthalimide, N-vinylpyrazolidone, butadiene, isoprene, vinylidene chloride, ethylene and the like. Sul-

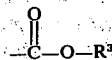
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foacrylate salts are particularly useful as comonomers in the practice of this invention. For example, sodium 3-methacryloyloxypropane-1-sulfonate, sodium 3-acryloyloxypropane-1-sulfonate, sodium 4-acryloyloxybutane-2-sulfonate and others as described in Dykstra, U.S. Pat. No. 3,411,911 issued Nov. 19, 1968.

As set out above, at least about 1% of each of the interpolymers useful in the practice of this invention is a monomer containing active methylene groups and having the structure



In this formula, R^1 is hydrogen, methyl or



R^2 and R^3 are independently selected from the group consisting of alkyl radicals, preferably alkyl radicals of from 1 to 10 carbon atoms, as exemplified by methyl, ethyl, propyl, butyl, hexyl, heptyl, octyl, nonyl, decyl; it is most preferred that where R^2 or R^3 are alkyl, they be of from 1 to 5 carbon atoms. R^2 and/or R^3 can also be cycloalkyl, preferably of from 5 to 7 carbon atoms, such as, for example, cyclopentyl, cyclohexyl or cycloheptyl; or aryl, preferably of from 6 to 12 carbon atoms, e.g., phenyl, naphthyl, unsubstituted or substituted with alkyl, carboxyl, alkoxy, carbonyl and the like, e.g., tolyl, xylyl, benzoyl, etc.

A particularly useful monomer containing an active methylene group according to this invention is ethyl acryloylacetate. This compound can be polymerized to advantage with one or more hydrophilic acrylic polymers as shown in the following preferred embodiments of this invention: a copolymer of ethyl acryloylacetate (20-25 weight percent) and acrylamide (80-95 weight percent); a copolymer of ethyl acryloylacetate (50 weight percent) and methacrylic acid (50 weight percent); and a terpolymer of ethyl acryloylacetate (5-20 weight percent), and N-(lower alkyl)acrylamide, e.g., N-isopropylacrylamide (5-20 weight percent), and a salt of sulfoacrylate, e.g., sodium 3-methacryloyloxypropane-1-sulfonate, (50-90 weight percent).

The preparation of ethyl acryloylacetate follows procedures as described by N. Nazarov and S. I. Zavyalov, Zh. Obshch. Khim., 23, 1793 (1953); and E. Wenhert, A. Afonso, J. B-Son Bredenberg, C. Kaneko and A. Tahara, J. Am. Chem. Soc., 86, 2038 (1964); G. Stork and R. Natix Guthikonda, Tetrahedron Letters, 27, 2755-58, (1972).

The temperature at which the interpolymers described herein are prepared is subject to wide variation since this temperature depends upon such variable features as the specific monomer used, duration of heating, pressure employed and like considerations. However, the polymerization temperature generally does not exceed about 110°C., and most often it is in the range of about 50 to about 100°C. The polymerization can be carried out in a suitable vehicle, for example, water or mixtures of water with water miscible solvents, as exemplified by methanol, ethanol, propanol, isopropyl alcohol, butyl alcohol, and the like. The pressure employed in the polymerization, if any, is usually only sufficient to maintain the reaction mixture

in liquid form, although either superatmospheric or subatmospheric pressures can be used where such use is advantageous. The concentration of polymerizable monomer in the polymerization mixture can be varied widely with concentrations up to about 40%, by weight, and preferably about 20 to about 40%, by weight, based on the weight of the vehicle, being satisfactory. Suitable catalysts for the polymerization reaction include, for example, the free radical catalysts, such as hydrogen peroxide, cumene hydroperoxide, water soluble azo type initiators and the like. In redox polymerization systems the usual ingredients can be employed. If desired, the polymer can be isolated from the reaction vehicle by freezing, salting out, precipitation or any other procedure suitable for this purpose.

As indicated in U.S. Pat. No. 3,142,568, issued July 28, 1964, it is sometimes advantageous to include a surface active agent or compatible mixtures of such agents in the preparation of vinyl or addition polymers and in coating photographic materials containing such polymers. Suitable wetting agents include the non-ionic, ionic and amphoteric types as exemplified by the polyoxyalkylene derivatives, amphoteric amino acid dispersing agents, including sulfobetaines and the like. Such wetting agents are disclosed in U.S. Pat. No. 2,600,831, issued June 17, 1952; U.S. Pat. No. 2,271,623 issued Feb. 3, 1942; U.S. Pat. No. 2,275,727 issued Mar. 10, 1942 and U.S. Pat. No. 2,787,604 issued Apr. 2, 1957; U.S. Pat. No. 2,816,920 issued Dec. 17, 1957 and U.S. Pat. No. 2,739,891 issued Mar. 27, 1956.

Dispersions of the photographic silver halide containing addition interpolymers containing active methylene groups, in combination with photographic binding agents, such as gelatin, can be made in a variety of ways. For example, an aqueous gelatin dispersion of the photographic silver halide can be mixed with an aqueous dispersion or solution of the interpolymer. Alternatively, the photographic silver halide can be precipitated in an aqueous dispersion or solution of the interpolymer with or without another colloid, depending upon the dispersing characteristics of the interpolymer. In this case, a water-soluble salt such as silver nitrate is admixed with a water-soluble halide such as potassium bromide in the presence of the mixture. In still another procedure, the photographic silver halide is precipitated in an aqueous gelatin solution and digested in the conventional manner known to the art. After digestion, but prior to coating, there is added to the emulsion an aqueous dispersion of the inter-polymer containing active methylene groups in its side chains. The bulk of the resulting dispersion can be increased by the addition of more of the interpolymer and/or natural or synthetic colloids or other binding agents suitable for use in photographic silver halide emulsions. Satisfactory colloids include, for example, gelatin, protein derivatives e.g. carboxy methylated proteins, colloidal albumin, cellulose derivatives, synthetic resins such as polyvinyl compounds e.g. polyacrylamide and the like.

The gelatin substitutes described herein can be employed in the binding agent in one or more layers of a photographic silver halide element. However, photographic silver halides are generally precipitated in the presence of binding agents such as gelatin or other colloids which exhibit very good peptizing action. Therefore, the photographic silver halide emulsions or layers of this invention will generally contain some binding agent such as gelatin which exhibits this very

good peptizing action. Generally, the concentration of the interpolymers described herein as gelatin substitutes will be in the range of about 20 to about 85%, often in the range of about 50 to about 85%, by weight, based on total binding agent (dry weight), employed in photographic emulsions, photographic emulsion layers or other layers of a photographic element. In the preferred case, the remainder of the binding agent is gelatin, although other colloids also give good results. Where the polymers are used in photographic elements in layers other than the emulsion layers, for example, in filter layers, antihalation layers, antiabrasion layers, antistatic layers, barrier layers, receiving layers for diffusion transfer processes and the like, they can be used as the sole vehicle or in admixture with natural or synthetic colloids such as are mentioned hereinbefore. The silver halide employed in the preparation of light sensitive coatings described herein includes any of the photographic silver halides as exemplified by silver bromide, silver chloride and silver iodide, or mixed silver halides such as silver chlorobromide, silver bromiodide, and the like. Very good results are obtained with high contrast silver halide emulsions in which the halide comprises at least 50 mole percent chloride. Preferred emulsions of this type contain at least 60 mole percent chloride; less than 40 mole percent bromide and less than 5 mole percent iodide.

The interpolymers described herein can also be incorporated into gelatin emulsions to provide an emulsion with increased hardness properties. The final resultant hardness of said emulsion is apparently dependent on the ratio of the gel in the emulsion and the absolute concentration of acryloyl units, which contain active methylene units, in the interpolymer.

The photographic compositions described herein can be coated on a wide variety of supports. Typical supports include polymeric films such as cellulose acetate film, polyvinyl acetal film, polystyrene film, polypropylene film and other polyolefin film, polycarbonate film, polyethylene terephthalate film and other polyester film as well as glass, paper, wood and the like. Supports such as paper which are coated with alpha-olefin polymers, particularly of alphaolefins containing 2-10 carbon atoms, as exemplified by polyethylene, polypropylene, ethylene-butene copolymers and the like, give good results.

The emulsions containing the interpolymers can be chemically sensitized with compounds of the sulfur group as described in Sheppard et al. U.S. Pat. No. 1,623,499 issued Apr. 5, 1927, noble metal salts such as gold salts, reduction sensitized with the reducing agents, and combinations of these. The interpolymers of this invention are especially useful to obtain hardened emulsions containing silver halides which have been chemically sensitized with gold and the like. The fog problems often associated with emulsions, such as gold sensitized emulsions which have been hardened by reducing hardeners such as formaldehyde, mucochloric acid and the like, are substantially reduced by the use of the interpolymer-gelatin emulsions which do not require reducing hardeners to achieve a hardened emulsion. However, the emulsion layers and other layers present in photographic elements made according to this invention can be hardened with any suitable hardener such as aldehyde, mucochloric acid and the like, aziridine hardeners, hardeners which are derivatives of dioxane, oxypolysaccharides such as oxystarch, oxy plant gums and the like. Such hardened layers will

have a melting point in water greater than about 150°F. and preferably greater than 200°F.

The emulsion can also contain additional additives, particularly those known to be beneficial in photographic emulsions, including for example, stabilizers or antifoggants, particularly the water-soluble inorganic acid salts of cadmium, cobalt, manganese and zinc as disclosed in U.S. Pat. No. 2,829,404, the substituted triazaindolizines as disclosed in U.S. Pat. Nos. 2,444,605 and 2,444,607, speed increasing materials, absorbing dyes, plasticizers and the like. Sensitizers which give particularly good results in the photographic compositions disclosed herein are the alkylene oxide polymers which can be employed alone or in combination with other materials, such as quaternary ammonium salts, as disclosed in U.S. Pat. No. 2,886,437 or with mercury compounds and nitrogen containing compounds, as disclosed in U.S. Pat. No. 2,751,299.

The interpolymers containing active methylene groups in their side chains can be used in various kinds of photographic emulsions. For example, they can be used in direct positive silver halide emulsions, x-ray and other non-spectrally sensitized emulsions as well as in orthochromatic, panchromatic and infrared sensitive emulsions, particularly those sensitized with merocyanine dyes, cyanine dyes, carbocyanine dyes and the like. Furthermore, these polymers can be used in emulsions intended for color photography, for example, emulsions containing color forming couplers or emulsions to be developed by solutions containing couplers or other color generating materials. In addition, these polymers can be used in photographic emulsions containing developers, e.g., polyhydroxybenzenes, as well as in emulsions intended for use in diffusion transfer processes which utilize the non-developed silver halide in the non-image areas of the negative to form a positive by dissolving the under-developed silver halide and precipitating it on a receiving layer in close proximity to the original silver halide emulsion layer. Such processes are described in Rott U.S. Pat. No. 2,352,014; Land U.S. Pat. No. 2,543,181 and Yackel et al. U.S. Pat. No. 3,020,155. The polymers described herein can also be used in color transfer processes which utilize the diffusion transfer of an image-wise 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. Color transfer processes of this type are described in Yutzy U.S. Pat. No. 2,856,142; Land et al. U.S. Pat. No. 2,983,606; Whitmore et al. British Pat. Nos. 904,364 and 840,731 and Whitmore et al. U.S. application Ser. No. 392,471, now U.S. Pat. No. 3,227,552. These polymers can also be used in unhardened colloid layers, particularly those designed for processing in hardening developers, as disclosed in British Pat. No. 825,544, published Dec. 16, 1959. Silver halide emulsions containing these polymers can be processed in mono-bath processes such as described in Haist et al. U.S. Pat. No. 2,875,048 or in stabilization type processes.

The following examples are included for a further understanding of the invention:

EXAMPLE 1 Copoly(acrylamide-ethyl acryloylacetate)

To a mixture of acrylamide (180 g, 2.53 mole) and ethyl acryloylacetate (20 g, 0.14 mole) in water (1600 ml) and absolute ethanol (125 ml), maintained under a

nitrogen atmosphere, was added 1.0 g 2,2'-azobis(2-methylpropionitrile). The solution was held at 65°C for 4 hours. To this mixture was added one liter of water and the product was precipitated from solution by the addition of isopropyl alcohol (10 gal.), filtered, washed, and dried. The yield of fluffy, white solid was 170 g.

The polymer composition consistent with the analysis, C, 47.4%; H, 7.6%; N, 17.3%, is 94 weight percent acrylamide and 6 weight percent ethyl acryloylacetate.

EXAMPLE 2 Terpoly(ethyl acryloylacetate-N-isopropyl acrylamide-3-methacryloyloxypropane-1-sulfonic acid sodium salt)

To a mixture of N-isopropylacrylamide (20.2 g, 0.18 mole), ethyl acryloylacetate (26.0 g, 0.18 mole) and 3-methacryloyloxypropane-1-sulfonic acid sodium salt (248.4 g, 1.08 mole) in water (2250 ml) and absolute ethanol (180 ml) under nitrogen atmosphere was added 2,2'-azobis(2-methylpropionitrile) (1.0 g) as initiator. The solution was heated at 65°C overnight. The product was precipitated from the resulting viscous solution in water with isopropanol (10 gal.), filtered, washed, and dried. The polymer had an inherent viscosity of 0.97 in 1 in normal sodium chloride solution.

EXAMPLE 3 Copoly(methacrylic acid-ethyl acryloylacetate)

To a mixture of methacrylic acid (10 g) and ethyl acryloylacetate (10 g) in acetone (40 ml) was added 2,2'-azobis(2-methylpropionitrile) (0.1 g) as initiator. The solution was heated at 65°C overnight. The polymer was isolated by precipitation in ether, filtered, and dried. The polymer had an inherent viscosity of 0.58 in methanol.

EXAMPLE 4

This example demonstrates that copoly(acrylamideethyl acryloylacetate) (weight ratio: 90/10), similar to the copolymer with weight ratio 94/6 described in Example 1, can be used as the vehicle for an all-polymeric photographic film which after exposure and processing yields sensitometric results which are quite similar to those obtained after dispersion of grains from the same emulsion in gelatin.

A high-speed silver bromoiodide (94:6) negative emulsion, similar to the type of emulsion described by Trivelli and Smith (PSA J. Vol. 79, 330), was prepared using as the peptizer poly(3-thiapentyl acrylate-co-3-acryloyloxypropane-1-sulfonic acid, sodium salt) (mole ratio 1:6). This polymeric peptizer contains a thioether group and was described in U.S. Pat. No. 3,615,624. Removal of soluble salts and concentration of the emulsion were carried out by ultrafiltration. After digestion to optimum speed, the emulsion was split into several parts, one of which was dispersed in copoly(acrylamide-ethylacryloylacetate) (weight ratio: 90/10) (160 g per silver mole), and another part in gelatin (160 g per silver mole). After admixture of customarily used adjuvants and of a crosslinking agent (2 g formaldehyde per 100 g of polymer or gelatin) both emulsions were coated on a transparent support so as to yield a coverage of 53.82 mg/dm² silver and 79.85 mg/dm² vehicle (polymer or gelatin, respectively). Exposure (500 W, 5400°K) and development (5 minutes in Kodak DK-50 Developer) (20°C) yielded

the following sensitometric results. Polymer "A" is copoly(acrylamide-ethyl acryloylacetate) (weight ratio: 90/10).

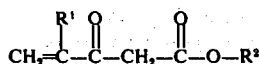
Vehicle	Relative Speed	Gamma	Net Fog (Total Fog Minus Base Density)
Polymer "A"	155	1.00	0.10
Gelatin	100	0.82	0.06

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

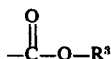
What is claimed is:

1. A photographic element comprising a support having coated thereon at least one photographic silver halide emulsion and at least one binding agent comprising a film-forming, addition interpolymer comprising

A. from about 1 to about 50% by weight of a polymerized monomer containing active methylene groups and having the formula



wherein R¹ is hydrogen, methyl or



and R² and R³ are alkyl radicals containing from 1 to 10 carbon atoms; and

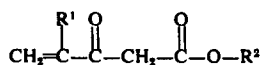
B. from about 50 to about 99% by weight of at least one additional polymerized ethylenically unsaturated monomer free of active methylene groups.

2. The element of claim 1 wherein the interpolymer has an inherent viscosity in the range of 0.75 to 2.0.

3. The element of claim 1 wherein at least one of the additional polymerized ethylenically unsaturated monomers is a sulfoacrylate salt.

4. The element of claim 3 wherein the sulfoacrylate salt is selected from the group consisting of sodium 3-methacryloyloxypropane-1-sulfonate, sodium 3-acryloyloxypropane-1-sulfonate and sodium 4-acryloyloxybutane-2-sulfonate.

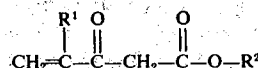
5. The element of claim 1 wherein the polymerized monomer of the formula



is ethyl acryloylacetate.

6. A photographic element comprising a support having coated thereon at least one photographic silver halide emulsion and at least one binding agent comprising a film-forming, addition interpolymer comprising

A. from about 1 to about 50% by weight of a polymerized monomer containing active methylene groups and having the formula

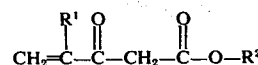


wherein R¹ is hydrogen or methyl and R² is an alkyl radical containing from 1 to 10 carbon atoms; and

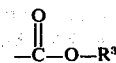
B. from about 50 to about 99% by weight of at least one additional polymerized ethylenically unsaturated monomer free of active methylene groups.

7. A photographic silver halide emulsion containing a binding agent comprising a film-forming, addition interpolymer comprising

A. from about 1 to about 50% by weight of a polymerized monomer containing active methylene groups and having the formula



wherein R¹ is hydrogen, methyl or



and R² and R³ are alkyl radicals containing from 1 to 10 carbon atoms; and

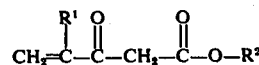
B. from about 50 to about 99% by weight of at least one additional polymerized ethylenically unsaturated monomer free of active methylene groups.

8. The emulsion of claim 7 wherein the interpolymer has an inherent viscosity in the range 0.75 to 2.0.

9. The emulsion of claim 7 wherein at least one of the additional polymerized ethylenically unsaturated monomers is a sulfoacrylate salt.

10. The emulsion of claim 9 wherein the sulfoacrylate salt is selected from the group consisting of sodium 3-methacryloyloxypropane-1-sulfonate, sodium 3-acryloyloxypropane-1-sulfonate and sodium 4-acryloyloxybutane-2-sulfonate.

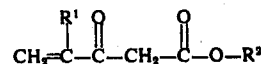
11. The emulsion of claim 7 wherein the polymerized monomer of the formula



is ethyl acryloylacetate.

12. A photographic silver halide emulsion containing a binding agent comprising a film-forming, addition interpolymer comprising

A. from about 1 to about 50% by weight of a polymerized monomer containing active methylene groups and having the formula



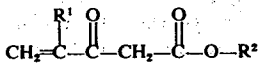
wherein R¹ is hydrogen or methyl and R² is an alkyl radical containing from 1 to 10 carbon atoms; and

B. from about 50 to about 99% by weight of at least one additional polymerized ethylenically unsaturated monomer free of active methylene groups.

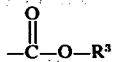
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13. A photographic element comprising a support having deposited thereon at least one photographic silver halide emulsion containing a binding agent comprising a film-forming, addition interpolymer comprising

A. from about 1 to about 50% by weight of a polymerized monomer containing active methylene groups and having the formula



wherein R¹ is hydrogen, methyl or



and R² and R³ are alkyl radicals containing from 1 to 10 carbon atoms; and

B. from about 50 to about 99% by weight of at least one additional polymerized ethylenically unsaturated monomer free of active methylene groups.

14. The element of claim 13 wherein the interpolymer has an inherent viscosity in the range 0.75 to 2.0.

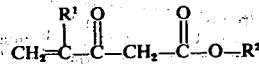
15. The element of claim 13 wherein at least one of the additional polymerized ethylenically unsaturated monomers is a sulfoacrylate salt.

16. The element of claim 15 wherein the sulfoacrylate salt is selected from the group consisting of sodium

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3-methacryloyloxypropane-1-sulfonate, and sodium 4-acryloyloxybutane-2-sulfonate.

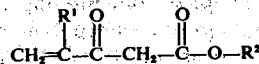
17. The element of claim 13 wherein the polymerized monomer of the formula



is ethyl acryloylacetate.

18. A photographic element comprising a support having deposited thereon at least one photographic silver halide emulsion containing a binding agent comprising a film-forming, addition interpolymer comprising

A. from about 1 to about 50% by weight of a polymerized monomer containing active methylene groups and having the formula



wherein R¹ is hydrogen or methyl and R² is an alkyl radical containing from 1 to 10 carbon atoms; and

B. from about 50 to about 99% by weight of at least one additional polymerized ethylenically unsaturated monomer free of active methylene groups.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,929,482

DATED : December 30, 1975

INVENTOR(S) : Ignazio S. Ponticello and Ernest J. Perry

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Title page, item [56], under UNITED STATES PATENTS, line 4, "3,632,341" should read ---3,632,342---.

Column 3, line 58, "alphabet" should read --- alpha-beta ---.

Column 4, line 33, "yxlyl" should read ---xylyl---.

Column 6, line 43, "alphaolefins" should read ---alpha-olefins ---.

Column 12, line 1, "methyacryloyloxypropane" should read ---methacryloyloxypropane---; and line 1, before "and" insert ---sodium 3-acryloyloxypropane-1-sulfonate---.

Signed and Sealed this

eleventh Day of May 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks