

[54] **HARDENABLE VEHICLES FOR SILVER HALIDE EMULSIONS**

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[52] U.S. Cl. **96/73; 96/76; 96/87 R; 96/114**

[51] Int. Cl.².. **G03C 1/76; G03C 1/48; G03C 1/78; G03C 1/72**

[58] Field of Search..... **96/73, 76, 114, 87 R**

[56] **References Cited**

UNITED STATES PATENTS

3,459,790	8/1969	Smith.....	260/483
3,488,708	1/1970	Smith.....	96/84
3,554,987	1/1971	Smith.....	260/79.3
3,700,456	10/1972	Smith.....	96/114
3,713,834	1/1973	Fitzgerald.....	96/114
3,775,129	11/1973	Dodwell.....	96/84
3,861,918	1/1975	Fitzgerald.....	96/114

Primary Examiner—Norman G. Torchin

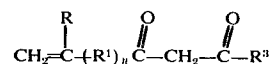
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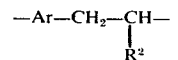
[57] **ABSTRACT**

Disclosed herein is a photographic element adapted for silver-dye bleach processes comprising a support having coated thereon at least one photographic silver halide emulsion and at least one binding agent comprising an interpolymer comprising

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



wherein n is 0 or 1, R is hydrogen or methyl, R¹ is substituted or unsubstituted aryleneethylene having the structure



wherein Ar is arylene, R² is hydrogen, alkyl, aryl, or cycloalkyl, R³ is alkoxy or amino when n is equal to 0, and R³ is alkyl, alkoxy, amino, cycloalkyl, or aryl when n is equal to 1; and

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

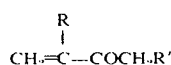
28 Claims, No Drawings

HARDENABLE VEHICLES FOR SILVER HALIDE EMULSIONS

This invention relates to the use of polymeric materials in photographic elements and emulsions to obtain a desirable combination of properties. In a preferred embodiment, this invention relates to photographic elements for silver-dye-bleach processes, especially those adapted for viscous "in-camera" processes.

Photographic elements employed in photography, particularly in the color print industry for the production of color photographs, must have good physical and photographic properties. Owing 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 the like conditions, and subject to hydrolysis to amino acid fragments when subjected to extremely acidic conditions. Many natural and synthetic materials have been proposed as substitutes or partial 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, U.S. Pat. No. 3,142,568, issued July 28, 1964 and U.S. patent application Ser. No. 394,002, filed Sept. 4, 1973, vinyl or addition polymers are employed as binding agents in layers of photographic elements to improve physical properties, including dimensional and chemical stability. However, the use of some polymers in layers of photographic elements, such as those described in U.S. Pat. No. 3,062,674 and U.S. Pat. No. 3,142,568, supra, 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 light-sensitive copolymer of the general formula



wherein R and R' 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. The copolymers of the Japanese patent, however, do not contain active methylene groups except wherein R' is acetyl. In that case the copolymer which is outside the scope of the present invention is not operable for the purposes of the present invention.

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 those 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 resulting in a loss of binding properties. U.S. patent application Ser. No. 497,803, filed of even date herewith by Ponticello and entitled "Poly-

mers Having Active Methylene Group" discloses cross-linkable polymers containing active methylene cross-linking sites in at least some of the side chains, wherein the group joining the side chain to the polymer backbone possesses increased resistance to hydrolysis. The use of certain of the polymers described above in photographic elements is disclosed in U.S. Ser. No. 394,002 filed Sept. 4, 1973.

Silver-dye-bleach processes are well known, having been described, for example, in J. S. Friedman, *History of Color Photography*, pp. 405-429, (1944) and A. Meyer, *The Journal of Photographic Science*, Vol. 13, pp. 90-97, (1965). These processes involve developing a silver halide emulsion containing bleachable dye, and bleaching the dye in just those areas where the silver has been developed. All of the silver ion is removed or rendered transparent and insensitive to light, leaving a dye-image in the areas where no metallic silver was present.

In most of the previously disclosed color photographic processes utilizing silver-dye-bleach, it was necessary to subject the exposed film to a large number of processing baths. Although these multistep silver-dye-bleach processes yield acceptable color pictures, the large number of steps together with the long processing time required prevented the utilization of such a process for an in-camera type development. Michel and Reitter, in U.S. Pat. No. 3,414,411, issued Dec. 3, 1968, disclosed an improved method of utilizing the silver-dye-bleach process which retained the advantages of the prior art, but eliminated the large number of processing steps and greatly reduced the time required to produce a color picture.

It is an object of this invention to provide improved binding agents for photographic layers such as photographic emulsions having excellent adhesion, color, hardening and sensitometric properties.

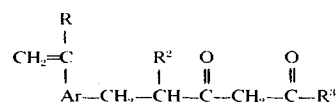
It is another object of this invention to provide improved photographic elements for silver-dye-bleach processes which are more stable to bleaching conditions which can be employed in such processes.

It is a further object of this invention to provide novel dye bleach materials suitable for in-camera processing.

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

In accordance with this invention, it has been found that an ethylenically unsaturated monomer containing an active methylene function can be polymerized with at least one additional monomer 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 an addition interpolymers comprising

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



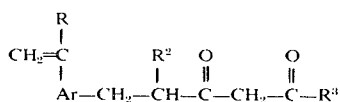
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wherein Ar is arylene, R is hydrogen or methyl, R² is hydrogen, alkyl, aryl, or cycloalkyl, and R³ is alkyl, alkoxy, amino, cycloalkyl, or aryl; and

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

As a preferred embodiment of the present invention, a photographic composition comprises at least one photographic silver halide emulsion and at least one binding agent comprising an addition interpolymer comprising

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

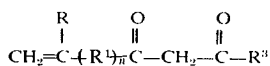


wherein Ar is arylene, R is hydrogen or methyl, R² is hydrogen, alkyl, aryl, or cycloalkyl, and R³ is alkyl, alkoxy, amino, cycloalkyl, or aryl; and

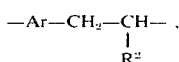
B. from 50 to about 99% by weight of at least one additional polymerized ethylenically unsaturated monomer.

In another aspect, the present invention comprises a photographic silver halide emulsion containing a bleachable dye containing a binding agent comprising an addition interpolymer comprising

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



wherein *n* is 0 or 1, R is hydrogen or methyl, R¹ is substituted or unsubstituted arylene having the structure

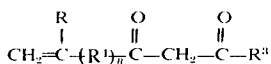


wherein R² is hydrogen alkyl, aryl, or cycloalkyl, R³ is alkoxy or amino when *n* is equal to 0, and R³ is alkyl, alkoxy, amino, cycloalkyl, or aryl when *n* is equal to 1; and

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

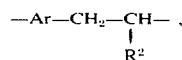
In still another, preferred, aspect, the present invention comprises a photographic element comprising a support having deposited thereon at least one photographic silver halide emulsion containing at least one bleachable dye, at least one hardener, and a binding agent comprising an addition interpolymer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

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



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wherein *n* is 0 or 1, R is hydrogen or methyl, R¹ is substituted or unsubstituted arylene having the structure

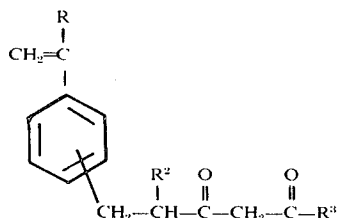


wherein R² is hydrogen alkyl, aryl, or cycloalkyl, R³ is alkoxy or amino when *n* is equal to 0, and R³ is alkyl, alkoxy, amino, cycloalkyl, or aryl when *n* is equal to 1; and

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

A particularly preferred embodiment comprises a photographic element comprising a support having deposited thereon at least one photographic silver halide emulsion containing at least one bleachable dye, at least one hardener and a binding agent comprising an addition interpolymer comprising

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



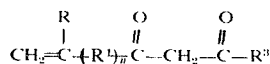
wherein R is hydrogen, or methyl, R² is hydrogen, alkyl, aryl, or cycloalkyl, and R³ is alkyl, amino, cycloalkyl, or aryl; and

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

The polymers employed in photographic materials according to the practice of this invention are addition interpolymers containing active methylene groups in the polymer side chains. Active methylene groups as described herein are methylene groups between two carbonyl groups. Such methylene groups exhibit unusual chemical activity and are said to be "active".

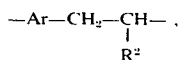
The molecular weights of the polymers employed in photographic emulsions and elements according to the practice of this invention are subject to a wide variation, but are often in the range of about 5000 to about 500,000. These polymers, which are generally water soluble, have inherent viscosities (0.25 g. polymer in 100 ml. 1 N. sodium chloride at 25°C.) from 0.10 to 2.0, preferably from about 0.25 to about 1.25.

As set out above, at least about 1% of each of the polymers useful in the practice of this invention with emulsions containing bleachable dyes is a polymerized monomer containing at least one active methylene group and having the structure



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wherein n is 0 or 1 and R is hydrogen or methyl, R¹ is substituted or unsubstituted aryleneethylene, having the structure



wherein Ar is an arylene, preferably of from 6 to 12 carbon atoms, e.g., phenyl, naphthyl, which can be substituted, if desired, with alkyl or alkoxy groups, preferably of from 1 to 10 carbon atoms, as exemplified by methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, and isomers thereof, methoxy, ethoxy, propoxy, butoxy, pentyloxy, etc. More preferably, where Ar is substituted, it is substituted with lower alkyl or alkoxy groups of from 1 to 5 carbon atoms. Ar also can have substituents which are cycloalkyl, preferably of from 5 to 7 carbon atoms, such as, for example, cyclopentyl, cyclohexyl, or cycloheptyl, cyano, halide, such as bromide, chloride, fluoride, and iodide, and others known to those skilled in the art. R² is hydrogen, alkyl, aryl, or cycloalkyl, as described above for the substituents of Ar.

When n is equal to 0, R³ can be alkoxy, preferably of from 1 to 10 carbon atoms; more preferably of from 1 to 5 carbon atoms, as described above for Ar substituents. When n is equal to 0, R³ also can be amino, having the structure



wherein R⁴ and R⁵ are hydrogen, alkyl, preferably having from 1 to 10 carbon atoms, substituted or unsubstituted cycloalkyl, preferably of from 5 to 7 carbon atoms, such as, for example, cyclopentyl, cyclohexyl, or cycloheptyl, or substituted or unsubstituted aryl,

preferably of from 6 to 12 carbon atoms as described above, e.g., phenyl, naphthyl and phenyloxy.

When n is equal to 1, R³ can be alkyl or alkoxy, each preferably having from 1 to 10 carbon atoms, as exemplified by methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, and isomers thereof, methoxy, ethoxy, propoxy, butoxy, pentyloxy, etc.; it is more preferred that where R⁴ is alkyl or alkoxy, it be of from 1 to 5 carbon atoms. When n is equal to 1, R³ also can be amino having the structure



wherein R⁴ and R⁵ are as defined above; or substituted or unsubstituted cycloalkyl, preferably of from 5 to 7

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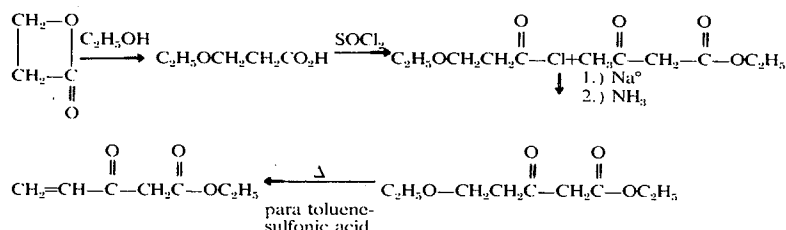
carbon atoms, such as, for example, cyclopentyl, cyclohexyl, or cycloheptyl; or aryl, preferably of from 6 to 12 carbon atoms, e.g., phenyl, naphthyl, unsubstituted or substituted with alkyl, carboxyl, alkoxycarbonyl and the like, e.g. tolyl, xylyl, benzyl, etc.

Three monomers containing active methylene groups particularly useful within the scope of this invention are ethyl 5-(m- and p-vinylphenyl)-3-oxopentanoate, 6-(m- and p-vinylphenyl)-2,4-hexanedione, and ethyl acryloylacetate. The first two monomers are mixtures of meta (60 wt. percent) and para (40 wt. percent) substituted isomers which are difficult to fractionate. The behavior of the mixture is similar to that of the individual isomeric compounds.

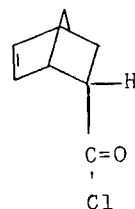
These monomers can advantageously be copolymerized with one or more other monomers, as shown in the following preferred embodiments of this invention: a copolymer of acrylamide (80 weight percent) and ethyl 5-(m- and p-vinylphenyl)-3-oxopentanoate (20 weight percent); a copolymer of acrylamide (80–95 weight percent) and 6-(m- and p-vinylphenyl)-2,4-hexanedione (20–5 weight percent); and a copolymer of N,N-dimethyl-N-2-hydroxypropylamine methacrylamide (85–90 weight percent) and 6-(m- and p-vinylphenyl)-2,4-hexanedione (15–10 weight percent).

The preparation of ethyl 5-(m- and p-vinylphenyl)-3-oxopentanoate and 6-(m- and p-vinylphenyl)-2,4-hexanedione follows procedures as described by C. R. Houser and T. M. Harris, *J. Amer. Chem. Soc.*, 80, 6360 (1958); and L. Weiler, *J. Amer. Chem. Soc.*, 92, 6702 (1970) and is described in Example 8 herein.

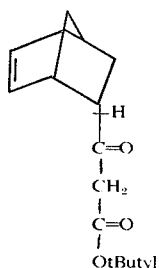
The preparation of ethyl acryloylacetate is described in I. N. Nazarov and S. I. Zavyalov, *Zh. Obshch. Khim.*, 23, 1703 (1953) and E. Wenkert, A. Afonso, J. B-son Bredenberg, C. Kaneko and A. Tahara, *J. Amer. Chem. Soc.*, 86, 2039 (1964) and follows the following reaction sequence shown below



The compound endo and exo-5-carbo-tert.-butoxy acetal-2-norbornene is prepared by adding n-butyllithium (2 moles) in tetrahydrofuran (2 liters) at 0°C and adding n-isopropylcyclohexylamine (2 moles). To this solution at -78°C was added dropwise tertiary butyl acetate over a period of 1 hour followed after thirty minutes by the acid chloride having the formula



(1 mole). The mixture was stirred at room temperature for 1 hour and then quenched with concentrated hydrochloric acid (300 ml) in water (700 ml). The mixture was allowed to reach room temperature and the organic layer was separated. The aqueous layer was extracted with ether and the combined extracts were washed with NaHCO_3 (500 ml) dried over anhydrous Mg SO_4 , filtered and the solvent removed. The residue was distilled giving the β -keto ester having the formula



The preparation of tertiary butyl acryloylacetate comprises adding the above keto ester over three to four hours at the top of a vertical quartz tube packed with quartz chips kept at 500°C . The crude product is collected under reduced pressure in a receiver cooled at -20°C . The material is immediately distilled.

The preparation of N,N-dimethylacryloylacetamide is carried out in the same manner as described above for the β -keto ester. However, the crude material is not distilled before simply pyrolyzing in the quartz tube.

As noted above, from 50 to 99% by weight of the polymers of this invention can comprise at least one additional polymerized ethylenically unsaturated monomer. 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, methacrylamide, vinyl chloride, methyl vinyl ketone, fumaric, maleic and itaconic esters, 2-chloroethylvinyl ether, acrylic acid, sodium methacryloyloxethyl sulfate, methacrylic acid, dimethyl-aminoethyl methacrylate, sodium 2-acrylamide-2-methylpropane-1-sulfonate, 2-hydroxyethyl methacrylate, 4,4,9-trimethyl-8-oxo-7-oxa-4-azonia-9-decene-1-sulfonate, N-vinylsuccinamide, N,N-dimethyl-N-2-hydroxypropylamine methacrylimide, N-vinylphthalimide, N-vinylpyrazolidone, butadiene, isoprene, vinylidene chloride, ethylene and the like. Sulfocrylate 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, 3-methyl-1-vinylimidazolium methosulfate, 1,2-dimethyl-5-vinylpyridinium methosulfate and others as described in Dykstra, U.S. Pat. No. 3,411,911 issued Nov. 19, 1968.

The temperature at which the polymers 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 ex-

ceed about 110°C ., and most often it is in the range of about 50° to about 100°C . The pressure employed in the polymerization is usually only sufficient to maintain the reaction mixture in liquid form, although either superatmospheric or subatmospheric pressures can be used where such is advantageous. The concentration of polymerizable monomer in the polymerization mixture can be varied widely with concentrations up to about 100% by weight and preferably from about 20 to about 70% by weight based on the weight of the polymerization mixture, 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 conventional 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 February 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 polymer. Alternatively, the photographic silver halide can be precipitated in an aqueous dispersion or solution of the polymer with or without another colloid, depending upon the dispersion characteristics of the polymer. 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 homopolymer or interpolymers containing active methylene groups in its side chains. The bulk of the resulting dispersion can be increased by the addition of more of the polymer 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, photo-

graphic 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 polymers described herein as gelatin substitutes will be in the range of about 20 to about 100%, more preferably in the range of about 50 to about 99%, 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, because it provides the advantage of allowing the coated layers to be chill set instead of heat dried. 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 bromoiodide, and the like. Very good results are obtained with high contrast silver halide emulsions in which the halide comprises at least 50 more 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 polymers 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 the active methylene units in the polymer.

The light-sensitive compositions described herein can be coated on a wide variety of supports, including film bases such as polyethylene terephthalate, cellulose acetate butyrate, polycarbonate, polyolefins (e.g., polyethylene, polypropylene) and the like. When such film bases are used, the photographic product obtained can be used, for example, as a transparency. If desired, the emulsions can be coated on an opaque support such as paper, polyolefin coated paper such as polyethylene or polypropylene coated paper which can be pigmented, with TiO_2 , for example, and electron bombarded to promote emulsion adhesion. When such supports are used, a color photographic print may be obtained.

The emulsions containing the homopolymers or 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 reducing agents, and combinations of these. The polymers 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, muco-

chloric acid and the like, are substantially reduced by the use of the polymer-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 aldehydes, bis(vinylsulfonyl) compounds, mucochloric acid and the like, aziridine hardeners, hardeners which are derivatives of dioxane, oxypolysaccharides such as oxystarch, oxy plant gums and the like. Useful concentrations of hardeners are related to the amount of polymeric binder used and are known to those skilled in the art. 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.

A detailed description of various emulsions in which the polymers can be used can be found in *Product Licensing Index*, publication no. 9232, December, 1971, pp. 107-110.

The polymers 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 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 emulsions 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.

In certain preferred embodiments, the polymers of this invention are used in photographic image-transfer film units such as in image-transfer film units as described, for example, in U.S. Pat. Nos. 2,543,181; 2,983,606; 3,227,550; 3,227,552; 3,415,645; 3,415,644; 3,415,646 and 3,635,707, Canadian Pat. No. 674,082 and Belgian Pat. Nos. 757,959 and 757,960, both issued Apr. 23, 1971 and British Pat.

Nos. 904,364 and 840,731. In highly preferred embodiments, the polymers are particularly useful in the photographic element of an image-transfer film unit which is designed to be processed with a single alkaline processing solution.

The polymeric materials of this invention are advantageously used in image-transfer elements wherein it is desired to process with a highly alkaline processing composition, and in those instances where the film unit remains laminated together after processing. The alkali resistant polymers of this invention are generally useful in image-transfer film units which comprise:

1. a photosensitive element comprising a support having thereon at least one layer containing a silver halide emulsion preferably having associated therewith an image dye-providing material and more preferably at least three of said layers which contain, respectively, a blue-sensitive silver halide emulsion, a green-sensitive silver halide emulsion and a red-sensitive silver halide emulsion;
2. an image-receiving layer which can be located on a separate support and superposed on said support containing said silver halide emulsions layers or, preferably, it can be coated on the same support adjacent to the photosensitive silver halide emulsion layers; and
3. means containing an alkaline processing composition adapted to discharge its contents within said film unit.

Where the receiver layer is coated on the same support with the photosensitive silver halide layers, the support is preferably a transparent support; an opaque layer is preferably positioned between the image-receiving layer and the photosensitive silver halide layer, and the alkaline processing composition preferably contains an opacifying substance such as carbon or a pH-indicator dye which is discharged into the film unit between a dimensionally stable support or cover sheet and the photosensitive element.

A means for containing the alkaline processing solution can be any means known in the art for this purpose, including rupturable containers positioned at the point of desired discharge of its contents into the film unit and adapted to be passed between a pair of juxtaposed rollers to effect discharge of the contents into the film unit, frangible containers positioned over or within the photosensitive element, hypodermic syringes, and the like.

The polymers described herein can also be used in azo dye transfer processes wherein, for example, a negative emulsion yields a positive image such as described in U.S. Pat. No. 2,728,290.

The term "image dye-providing material" as used herein is understood to refer to those compounds which either (1) do not require a chemical reaction to form the image dye or (2) undergo reactions encountered in photographic imaging systems to produce an image dye, such as with color couplers, oxichromic compounds and the like. The first class of compounds is generally referred to as preformed image dyes and includes shifted dyes, etc., while the second class of compounds is generally referred to as dye precursors.

The terms "initially diffusible" and "initially immobile" as used herein refer to compounds which are incorporated in the photographic element and, upon contact with an alkaline processing solution, are sub-

stantially diffusible or substantially immobile, respectively.

The image dye-providing materials, in one preferred embodiment where negative silver halide emulsions are used, can be initially mobile image dye-providing materials such as those used in image-transfer photographic elements. Typical useful, initially mobile image dye-providing materials include dye developers as disclosed in U.S. Pat. Nos. 2,983,606; 3,255,001 and the like; oxichromic developers which undergo chromogenic oxidation to form image dyes as disclosed in U.S. Ser. No. 308,869 filed Nov. 22, 1972; shifted indophenol dye developers is disclosed in Bush and Reardon, U.S. Ser. No. 227,113 filed Feb. 17, 1972 and now U.S. Pat. No. 3,854,945; metalized dye developers as disclosed in U.S. Pat. Nos. 3,482,972; 3,544,545; 3,551,406 and 3,563,739; and the like; all of which are incorporated herein by reference.

In another embodiment, immobile image dye-providing compounds can be used in association with silver halide emulsions wherein said compounds undergo oxidation followed by hydrolysis to provide an imagewise distribution of a mobile image dye. Compounds of this type can be used with negative emulsions to form positive image records in the exposed photographic element, or they can be used with direct-positive or reversal emulsions to form positive transfer images such as in an image-transfer film unit. Typical useful compounds of this type are disclosed in Canadian Pat. No. 602,607 by Whitmore et al. issued Aug. 2, 1960, U.S. Ser. Nos. 351,673 by Fleckenstein et al. and 351,700 by Fleckenstein, both filed Apr. 16, 1973, and 160,068 by Gompf et al., now U.S. Pat. No. 3,698,897 and U.S. Pat. Nos. 3,728,113 by Becker et al., 3,725,062 by Anderson et al., 3,227,552 by Whitmore, 3,443,939; 3,443,940 and 3,443,941, and the like, all of which are incorporated herein by reference.

In a particularly preferred embodiment, the photographic elements described herein contain bleachable dyes, preferably non-diffusible dyes, of the type well known in the art. The term "bleachable dyes" as used herein includes compounds which are dye precursors, i.e., compounds which become colored during processing of the photographic material. The term "non-diffusible" as used herein refers to bleachable dyes which in themselves are non-diffusible in the emulsion, or dyes which are rendered non-diffusible by the use of a suitable mordant, such as those described in U.S. Pat. No. 2,882,156. The elements of this invention can have a single emulsion coating for monochrome dye images formed from either one or a mixture of azo dyes, which dye images are either colored or neutral (e.g., black and white) images. Primarily, azo dyes are used in silver-dye-bleach systems because the bleaching process cleaves the —N=N— double bond to give two aromatic fragments. Typical azo dyes which can be used in the practice of this invention are listed in numerous patents, some of which are United Kingdom Pat. Nos. 923,265; 999,996; 1,042,300; 1,077,628; U.S. Pat. Nos. 3,178,290; 3,178,291; 3,183,225 and 3,211,556.

Bleachable dyes include those known in the art and dyes such as disclosed in the Color Index (third edition) published by the Society of Dyes and Colorists, copyright 1971, printed by Lund Humphreys, Bradford and London, provided they are bleachable as herein described. This includes bleachable dyes such as azo dyes, formazan dyes and others known to one skilled in

the art. Bleachable dyes known in the art include organic residues such as —N=N— and —NO₂, etc. including metalized versions of these dyes. Precursors to these dyes as known in the art, such as, hydrazo or diazonium compounds to yield azo dyes, tetrazolium salts to yield formazan dyes, etc., are also useful herein.

The bleachable dyes are defined as those dyes which in the presence of a photographic image comprised of silver metal and an aqueous solution of a silver complexing agent such as thiourea and an electron transport agent such as phenazine at pH values less than 4.0 suffer discharge of their color proportionate to the amount of silver metal present. Further examples of these dyes may be found in U.S. Pat. No. 3,202,511; U.S. Pat. No. 3,493,372; Great Britain Pat. No. 1,146,118 and Great Britain Pat. No. 1,255,857.

The elements of this invention may have a plurality of coatings each containing a different bleachable dye for providing multicolor images. Especially useful arrangements are those in which at least three light-sensitive emulsion layers are provided which are respectively sensitized to blue, green and red radiation, and containing, respectively, nondiffusible yellow, ma-

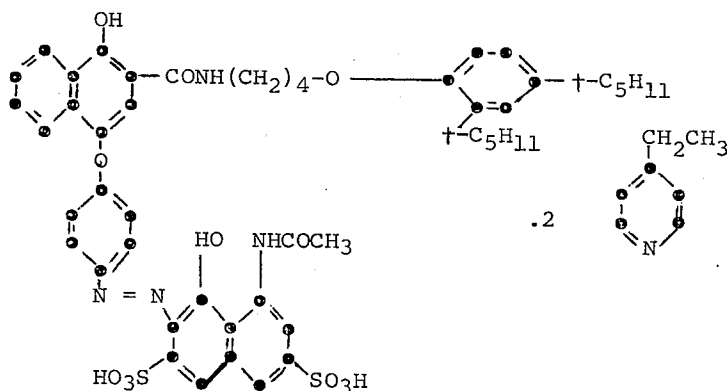
2,183,395 and 2,270,118. The catalyst may be incorporated in the emulsion, the alkaline processing material, an acidic processing web, or in more than one, or all of these elements. These compounds oxidize the metallic silver to silver ion, and in so doing are reduced. The reduced catalyst then cross-oxidizes with the image dye. This cross-oxidation decolorizes (i.e., bleaches) the image dye and oxidizes the catalyst back to its original state.

The silver dye bleachable elements of this invention are particularly advantageous in the resistance to hydrolysis at pH values less than 4.0 during the dye bleach reaction. This includes conditions of high temperatures and prolonged contact. Resistance to hydrolysis is demonstrated at temperatures up to 150°C for 60 seconds or for one month at room temperature at pH values of less than 1.0.

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

EXAMPLE 1

A series of coatings on a polyester film support comprising the azo dye having the structure



genta and cyan dyes. The emulsions used in this invention can contain the bleachable dyes. However, it is also possible, and sometimes preferable, to incorporate the bleachable dye in an alkali-permeable layer contiguous to the emulsion layer. This arrangement provides increased speed, especially when the bleachable dye containing layer is coated under the emulsion layer. Thus, in one useful arrangement a support has coated thereon, in the following order, layers containing, respectively, blue-sensitive silver halide; bleachable yellow dye; green-sensitive silver halide; bleachable magenta dye; red-sensitive silver halide; and bleachable cyan dye.

Conventional photographic developers are operable in this invention. These developers can be incorporated in emulsions in accordance with prior art procedures, or can be added to the alkaline processing solution. In certain instances, it is possible to incorporate in the emulsion one molecule which contains both the developing function and the bleachable dye function. Such molecules are non-diffusible and the dye portion of the molecule must be bleachable.

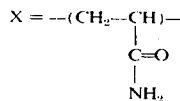
The bleaching of the image dye is conducted in the presence of a suitable catalyst, such as a phenazine, a quinoxaline or an anthraquinone. A number of catalysts useful herein are described in U.S. Pat. Nos.

dispersed in various vehicles within the scope of this invention were prepared as identified in Table I.

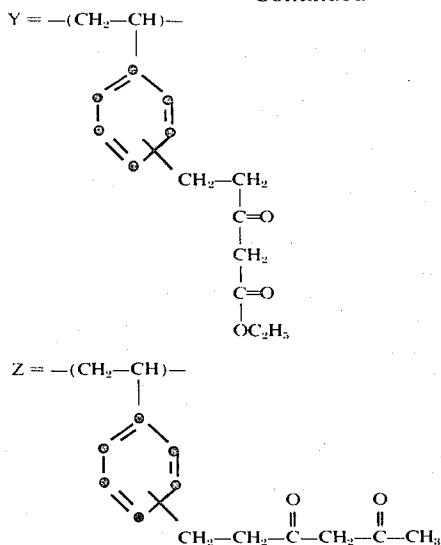
Table 1

Sample No.	Vehicle	Conc. mg/ft ² (mg/dm ²)	Formaldehyde Hardener mg/ft ² (mg/dm ²)
1 (Control)	Gelatin	250 (26.9)	2.5 (0.269)
2 (Control)	Gelatin	250 (26.9)	25.0 (2.69)
3	XY-80	250 (26.9)	2.5 (0.269)
4	XY-80	250 (26.9)	25.0 (2.69)
5	XZ-90	250 (26.9)	2.5 (0.269)
6	XZ-90	250 (26.9)	25.0 (2.69)
7	XZ-80	250 (26.9)	2.5 (0.269)
8	XZ-80	250 (26.9)	25.0 (2.69)

The materials used as vehicles are identified as having the following structures:



-Continued



The numbers used with the vehicle identification letters refer to the weight percent of material X based on the total polymer weight if the polymerization went to 100% conversion.

Procedure: To test the polymeric vehicles, samples were brought to pH .8 with a suitable acid and then heated for 10 seconds at 100°C. The coatings were cooled and washed in water and the dye coatings evaluated for reticulation and adhesion.

Results: No adhesion of the dye layer to its support was observed with Sample 1, and complete degradation of the gelatin vehicle had occurred. In Sample 2, which employed gelatin and a higher level of formaldehyde, some degradation and loss of gelatin had occurred, but the results were improved. In the remaining Samples 3 through 8, the dyed layer remained intact with no apparent degradation of the vehicles.

EXAMPLE 2

Additional samples were prepared and tested as in Example 1 but containing, in combination, 125 mg/ft² (13.5 mg/dm²) gelatin and 125 mg/ft² (13.5 mg/dm²) of the polymers described in Samples 3 through 8 of Table I. The results showed that some degradation of the vehicle was apparent. Each sample, however, was superior to the controls which contained only gelatin.

EXAMPLE 3

A series of photographic silver halide elements was prepared as in Example 1, but which also contained a silver chlorobromide emulsion coated at 40 mg Ag/ft² (4.31 mg/dm²) in the same layer. Separate samples of each of the coatings were then exposed, developed for 1 minute at 23°C with a metol-hydroquinone high contrast negative developer (Kodak Developer D-19), fixed, washed, and dried. The silver images and overall dye densities were the same in all samples. Samples of each coating were then dye bleached with thiourea (100 g/l), HCl concentrated (100 g/l) and phenazine (20 mg/l) and bleached dye image quality was observed.

The results indicated that prolonged times were required to obtain dye images in the elements containing the polymers of this invention; however, the images obtained were much superior to those of the gelatin-

containing controls due to lower reticulation or gelatin softening.

EXAMPLE 4

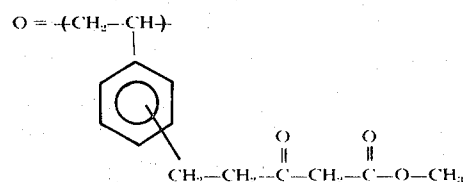
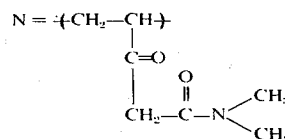
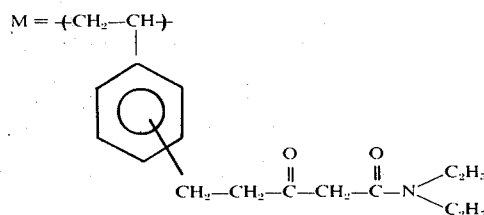
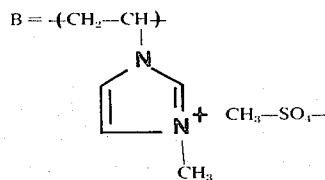
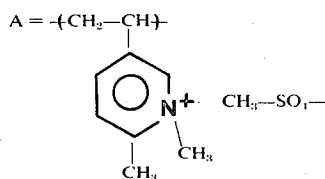
Separate exposed and developed samples of the elements prepared according to Example 3 were dye bleached at 23°C with an aqueous viscous processing solution. The viscous processing composition contained:

	g/l H ₂ O
3,6-Dithiaoctane-1,8-diol	100
p-Toluenesulfonic acid	100
Phenazine	0.02
Hydroxyethyl cellulose	4.0

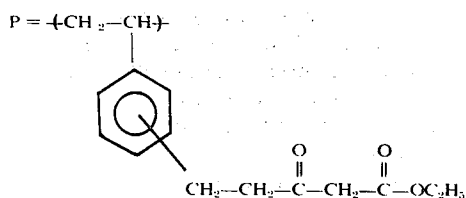
Results: Within 24 hours, the control samples comprising gelatin as the vehicle were unrecognizable owing to the hydrolysis of the gelatin. Images, and the vehicles, of all coatings containing the non-hydrolyzable polymers of this invention remained intact.

EXAMPLE 5

Example 4 was repeated using the following polymers:



-Continued



In ratios and coating structures as follows:

AY	90:10
BZ	90:10
BY	90:10
XM	90:10
XO	90:10
XP	80:20
XN	90:10

One series of coating structures contained 125 mg/ft² of polymer and gelatin and another contained 250 mg/ft² of polymer with only sufficient gelatin to peptize the silver halide emulsion. The hardener was 1% formalin. The results were substantially identical to those obtained in Example 4.

EXAMPLE 6

Additional dye/vehicle coatings as described in Example 1 were prepared but the formaldehyde hardener employed therein was replaced with equal weights of bis-vinyl sulfone methyl ether. The testing procedure of Example 1 was carried out and the results compared to those of Example 1. Slight differences were apparent, but the sulfone hardener indicated some improvement for gelatin, while formaldehyde was more appropriate for the polymeric coatings.

EXAMPLE 7

The following listed vehicles comprising varying concentrations of hardenable moieties were coated and tested according to the procedure of Example 3.

Polymer	Wt. % of Hardenable Moiety
XZ-95	5
XZ-90	10
XZ-85	15
XZ-80	20

wherein X and Z are as in Example 1.

The results improved with increasing amounts of hardenable moieties. No adverse effects were observed with respect to silver development or silver-dye bleaching.

EXAMPLE 8

Preparation of 6-(m- and p-vinylphenyl)-2,4-hexanedione

To a suspension of sodium hydride (41.3 g, 1M, 57% oil dispersion) in tetrahydrofuran (2 liters) at 0° to 10°C was added 2,4-pentanedione (100 g, 1M) and the solution was stirred at 0°C for 15 minutes, then N-butyl lithium (1M) in hexane was added slowly at 0° to 10°C and the solution of the dianion was stirred at 0°C for an additional 15 minutes. Vinylbenzylchloride (obtained from the Dow Chemical Company as a mixture of meta 60% and para 40% isomers (152.5 g, 1M)) was added at 0°C and the reaction mixture was stirred at room temperature for 1 to 2 hours. The mixture was

poured onto cracked ice containing hydrochloric acid (200 ml). The organic layer was separated and the aqueous layer was extracted with chloroform (5 × 150 ml). The combined organic extracts were washed with saturated bicarbonate solution (250 ml), saturated chloride solution (250 ml) and water (250 ml), dried, filtered and the solvent removed.

The residual oil was diluted with an equal volume of methanol and poured into a large excess of hot copper acetate solution (200 g in 1750 liters of water). The copper chelate fell out, was filtered off and washed with water followed by ligroin (1 liter). The copper chelate was then decomposed in the presence of ice cold 10% sulfuric acid and the mixture extracted with ether (5 × 200 ml). The ether extracts were washed with saturated bicarbonate solution (2 × 250 ml), saturated sodium chloride solution (250 ml) and water (250 ml), dried, filtered and the solvent removed. The residue was distilled giving 6-(m- and p-vinylphenyl)-2,4-hexanedione boiling at 77° to 82°C at 0.005 mm. The yield was 65%. With analysis, the amount of carbon in the final product was 77.7 weight percent as compared to 77.8 theoretical. The amount of hydrogen in the final product was 7.6 weight percent as compared to 7.4 percent theoretical.

EXAMPLE 9 (Control)

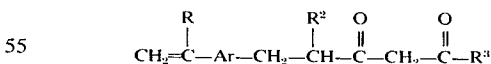
Dye/vehicle coatings were prepared and tested as described in Example 1. One set of samples was a repeat of Samples 1 and 2, which contained gelatin as the vehicle, and a second set of samples contained poly(N-isopropylacrylamide-co-3-methacryloyl-oxypropane-1-sulfonic acid, sodium salt-coacetoxethyl methacrylate) (54:31.5:14.5 weight percent, respectively), which is outside the scope of this invention. This polymer, although a generally good emulsion vehicle, performed like the gelatin control in the dye-bleach tests and, in all cases, degradation of the vehicles was observed.

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 an addition interpolymer comprising

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



wherein Ar is arylene, R is hydrogen or methyl, R² is hydrogen, alkyl, aryl, or cycloalkyl, R³ is alkoxy or amino when n is equal to 0, and R³ is alkyl, alkoxy, amino, cycloalkyl, or aryl when n is equal to 1; and

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

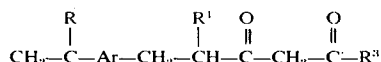
2. The element of claim 1 wherein the polymer has an inherent viscosity in the range of 0.1 to 2.0.

3. The element of claim 1 wherein at least one of the additional polymerized ethylenically unsaturated monomers is selected from the group consisting of acrylam-

ide, N-butyl acrylate, 2-hydroxyethyl methacrylate, N-isopropyl acrylamide, methacrylic acid, vinylimidazole, and N,N-dimethyl-N-2-hydroxypropylamine methacrylimide, sodium 2-acrylamide-2-methylpropane-1-sulfonate, sodium p-styrene sulfonate, 3-methyl-1-vinylimidazolium methosulfate and 1,2-dimethyl-5-vinylpyridinium methosulfate.

4. The element of claim 3 wherein at least one of the additional polymerized ethylenically unsaturated monomers is acrylamide.

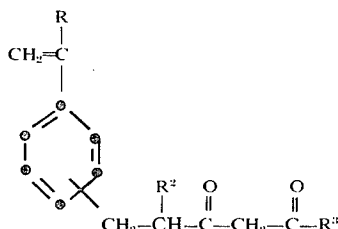
5. The element of claim 1 wherein the polymerized monomer of the formula



is selected from the group consisting of t-butyl 5-(m- and p-vinylphenyl)-3-oxopentanoate, N,N-diethyl-5-(m- and p-vinylphenyl)-3-oxopentanoic acid amide, ethyl 5-(m- and p-vinylphenyl)-3-oxopentanoate, and 6-(m- and p-vinylphenyl)-2,4-hexanedione.

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

A. from about 1 to about 50% by weight of a polymerized monomer containing at least one active methylene group having the formula

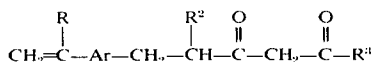


wherein R is hydrogen or methyl, R² is hydrogen, and R³ is alkyl or alkoxy; and

B. from about 50 to about 99% weight of at least one additional polymerized ethylenically unsaturated monomer.

7. A photographic silver halide emulsion containing a binding agent comprising an addition interpolymer comprising

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



wherein R is hydrogen or methyl, Ar is substituted or unsubstituted arylene, R² is hydrogen, alkyl, aryl, or cycloalkyl, R³ is alkoxy, amino, cycloalkyl, or aryl; and

B. From 50 to about 99% by weight of at least one additional polymerized ethylenically unsaturated monomer.

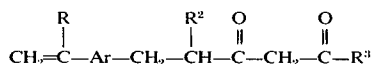
8. The emulsion of claim 7 wherein the interpolymer has an inherent viscosity in the range of 0.10 to 2.0.

9. The emulsion of claim 7 wherein at least one of the additional polymerized ethylenically unsaturated monomers is selected from the group consisting of acrylam-

ide, N-butyl acrylate, 2-hydroxyethyl methacrylate, N-isopropylacrylamide, methacrylic acid, vinylimidazole, and N,N-dimethyl-N-2-hydroxypropylamine methacrylimide, sodium 2-acrylamide-2-methylpropane-1-sulfonate, sodium p-styrene sulfonate, 3-methyl-1-vinylimidazolium methosulfate and 1,2-dimethyl-5-vinylpyridinium methosulfate.

10. The emulsion of claim 9 wherein at least one of the additional polymerized ethylenically unsaturated monomers is acrylamide.

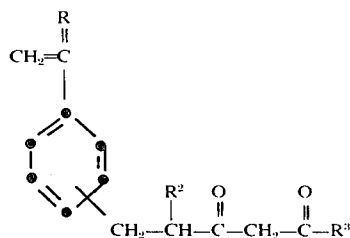
11. The emulsion of claim 7 wherein the polymerized monomer of the formula



is selected from the group consisting of t-butyl 5-(m- and p-vinylphenyl)-3-oxopentanoate, N,N-diethyl-5-(m- and p-vinylphenyl)-3-oxopentanoic acid amide, ethyl 5-(m- and p-vinylphenyl)-3-oxopentanoate, and 6-(m- and p-vinylphenyl)-2,4-hexanedione.

12. A photographic silver halide emulsion containing a binding agent comprising an addition interpolymer comprising

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

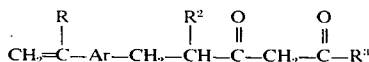


wherein R is hydrogen or methyl, R² is hydrogen, and R³ is alkyl or alkoxy; and

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

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

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



wherein R is hydrogen or methyl, Ar is substituted or unsubstituted arylene, R² is hydrogen, alkyl, aryl, or cycloalkyl, R³ is alkyl, alkoxy, amino cycloalkyl, or aryl; and

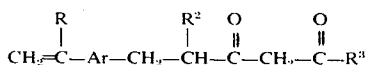
B. from 50 to about 99% by weight of at least one additional polymerized ethylenically unsaturated monomer.

14. The element of claim 13 wherein the interpolymer has an inherent viscosity in the range of 0.10 to 2.0.

15. The element of claim 13 wherein at least one of the additional polymerized ethylenically unsaturated monomers is selected from the group consisting of acrylamide, N-butyl acrylate, 2-hydroxyethyl methacrylate, N-isopropylamide, methacrylic acid, vinylimidazole, N,N-dimethyl-N-2-hydroxypropylamine methacrylimide, sodium 2-acrylamido-2-methylpropane-2-sulfonate, sodium p-styrene sulfonate, 3-methyl-1-vinylimidazolium methosulfate and 1,2-dimethyl-5-vinylpyridinium methosulfate.

16. The element of claim 15 wherein at least one of the additional polymerized ethylenically unsaturated monomers is acrylamide.

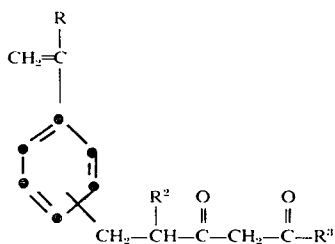
17. The element of claim 13 wherein the polymerized monomer of the formula



is selected from the group consisting of t-butyl 5-(m- and p-vinylphenyl)-3-oxopentanoate, N,N-diethyl-5-(m- and p-vinylphenyl)-3-oxopentanoic acid amide, ethyl 5-(m- and p-vinylphenyl)-3-oxopentanoate, and 6-(m- and p-vinylphenyl)-2,4-hexanedione.

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

A. from about 1 to about 50% by weight of a polymerized monomer containing at least one active methylene group having the formula

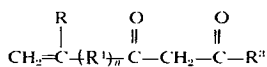


wherein R is hydrogen or methyl, R² is hydrogen, and R³ is alkyl or alkoxy; and

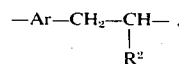
B. from about 50 to about 99% by weight of at least one additional polymerized ethylenically unsaturated monomer.

19. A photographic element adapted for silver-dye-bleach processes comprising a support having coated thereon at least one photographic silver halide emulsion, at least one bleachable dye, at least one hardener, and at least one binding agent comprising an addition interpolymer comprising

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



wherein n is 0 or 1, R is hydrogen or methyl, R¹ is substituted or unsubstituted aryleneethylene having the structure



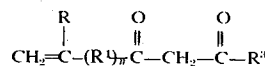
wherein Ar is arylene, R² is hydrogen, alkyl, aryl, or cycloalkyl, R³ is alkoxy or amino when n is equal to 0, and R³ is alkyl, alkoxy, amino, cycloalkyl, or aryl when n is equal to 1; and

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

20. The element of claim 19 wherein the interpolymer has an inherent viscosity in the range of 0.10 to 2.0.

21. The element of claim 19 wherein at least one of the additional polymerized ethylenically unsaturated monomers is selected from the group consisting of acrylamide, N-butyl acrylate, 2-hydroxyethyl methacrylate, N-isopropylacrylamide, methacrylic acid, vinylimidazole, N,N-dimethyl-N-2-hydroxypropylamine methacrylimide, sodium 2-acrylamido-2-methylpropane-2-sulfonate, sodium p-styrene sulfonate, 3-methyl-1-vinylimidazolium methosulfate and 1,2-dimethyl-5-vinylpyridinium methosulfate.

22. The element of claim 19 wherein the polymerized monomer of the formula



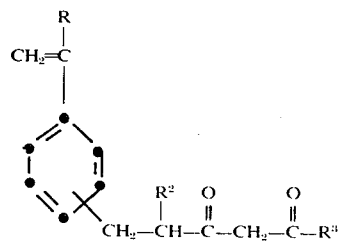
is selected from the group consisting of t-butyl 5-(m- and p-vinylphenyl)-3-oxopentanoate, N,N-diethyl-5-(m- and p-vinylphenyl)-3-oxopentanoic acid amide, ethyl acryloylacetate, ethyl 5-(m- and p-vinylphenyl)-3-oxopentanoate, 6-(m- and p-vinylphenyl)-2,4-hexanedione, tert-butyl acryloylacetate, and N,N-dimethylacryloylacetamide.

23. The element of claim 19 wherein the hardener is selected from the group consisting of bis-vinyl sulfone methyl ether and formaldehyde.

24. The element of claim 19 wherein the bleachable dye is an azo dye.

25. A photographic element adapted for silver-dye-bleach processes comprising a support having coated thereon at least one photographic silver halide emulsion, at least one azo dye, at least one hardener, and at least one binding agent comprising an addition interpolymer comprising

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



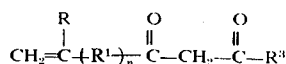
wherein R is hydrogen or methyl, R² is hydrogen, and R³ is alkyl or alkoxy; and

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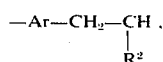
B. from about 50 to about 99% by weight of at least one additional polymerized ethylenically unsaturated monomer.

26. A photographic silver halide emulsion containing a bleachable dye and a binding agent comprising an addition interpolymer comprising

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



wherein n is 0 or 1, R is hydrogen or methyl, R^1 is substituted or unsubstituted aryleneethylene having the structure



wherein Ar is arylene, R^2 is hydrogen, alkyl, aryl, or cycloalkyl, R^3 is alkoxy or amino when n is equal to 0, and R^3 is alkyl, alkoxy, amino, cycloalkyl, or aryl when n is equal to 1; and

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

27. In an image-transfer film unit comprising

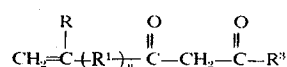
A. a photosensitive element comprising a support having thereon at least one layer containing a silver halide emulsion,

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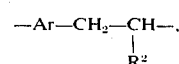
B. an image-receiving layer, and

C. means containing an alkaline processing composition adapted to discharge its contents within said film unit, the improvement wherein at least one of the alkali permeable layers contains a polymer comprising

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



wherein n is 0 or 1, R is hydrogen or methyl, R^1 is substituted or unsubstituted aryleneethylene having the structure



wherein Ar is arylene, R^2 is hydrogen, alkyl, aryl, or cycloalkyl, R^3 is alkoxy or amino when n is equal to 0, and R^3 is alkyl, alkoxy, amino, cycloalkyl, or aryl when n is equal to 1; and

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

28. An image transfer film unit according to claim 27 wherein said silver halide emulsion has associated therewith an image dye providing material.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,904,418

DATED : September 9, 1975

INVENTOR(S) : Rowland George Mowrey and Ignazio Salvatore
Ponticello

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

Column 2, lines 2-3, "corsslinking" should read --crosslinking--

vinylpyrrolidone--. Column 10, line 45, after "dyes" (first occurrence), --,-- should be inserted. Column 12, line 13, "is" should read --as--. Column 18, line 32, that part of formula reading "isopropylacrylamideco" should read --isopropylacrylamide-co--; line 33, that part of formula reading "coacetoacetoxyethyl" should read --co-acetoacetoxyethyl--; line 62, "ethyleneically" should read --ethylenically--. Column 19, line 43, after "99%", --by-- should be inserted. Column 20, line 49, "at binding" should read --a binding--. Column 24, line 8, "activity" should read --active --.

Signed and Sealed this

Sixth Day of July 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks