

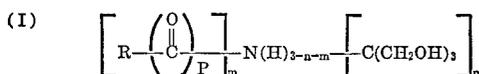


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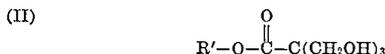
The art would be greatly enhanced by hydrophilic colloid-containing compositions which could effectively, economically and conveniently utilize the advantages of relative flexibility, toughness, rigidity, lack of dimensional change and the like possessed by elements having combined therein, the tempering agents such as the simple organic polyol toughener compounds disclosed. The unexpected advantages would be derived from the combination of substances which produce physical and sensitometric stability such as density on drying of colloid-containing systems while still providing significant tempering of the colloids contained in various of the coated layers such as emulsions.

## SUMMARY OF THE INVENTION

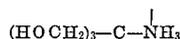
This invention relates to improving the characteristics of compositions containing a hydrophilic colloid like gelatin such as those comprising a photographic silver halide and a hydrophilic colloid tempering addendum such as a simple alcohol, like an alkyl substituted polyol. These addends toughen the colloid layers and substantially eliminate lack of shape and integrity, such as the mushiness imparted by other addenda like the covering power agents, while still retaining said increase in covering power. The class of tempering agent compounds unexpectedly found to provide these advantages has the formulae:



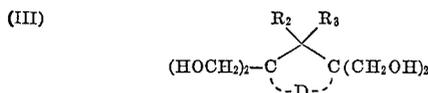
wherein R is phenyl, substituted phenyl such as o-methoxyphenyl, 2,4-dichlorophenyl, p-tolyl, p-bromophenyl, 2,4-xylyl, p-acetylphenyl, p-biphenyl and the like; alkyl of up to 8 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, hexyl, octyl and the like; substituted alkyl such as hydroxymethyl, methoxymethyl, hydroxyethyl, 3-chloropropyl, benzyl, and the like; or alkenyl such as vinyl, allyl, butadienyl, and the like; p is 0 or 1; m is 0, 1 or 2; and n is 1 or 2; the sum of m and n being at most 3; or



wherein R' is an alkyl group of from 1 to 8 carbon atoms such as ethyl, propyl, butyl, pentyl, hexyl, octyl and the like; a hydrogen atom, an alkali metal such as sodium, potassium and the like or the atoms necessary to complete an ammonium salt group, especially the organic ammonium salt group

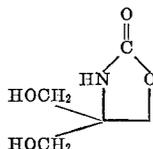


or

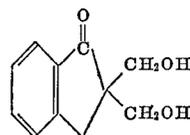


wherein D is the atoms needed to complete a 5 or 6 membered carbocyclic ring such as a cyclopentane or cyclohexane ring for example; optionally having a 6-membered alicyclic or aromatic ring fused thereto such as a benzocycloheptane, benzocyclohexane, perhydronaphthalene, or a perhydroindan fused ring group; taken separately R<sub>2</sub> is hydrogen and R<sub>3</sub> is hydroxy, or taken together R<sub>2</sub> with R<sub>3</sub> represents an oxo-group or

(IV)



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or  
(V)

A number of compounds within the above formulae exhibit especially good properties and are particularly effective tempering addends. For example among those hydroxyalkylaminoalkane polyols having Formula I are

2-(2-hydroxyethylamino)-2-hydroxymethyl)-1,3-propanediol or

2[bis(2-hydroxyethyl)amino]-2-(hydroxymethyl)-1,3-propanediol.

Among the oxo-compounds of structural Formula III preferred compounds are those wherein D forms a 6-membered ring optionally having a ring fused thereto such as

2,2,6,6-tetramethylcyclohexanol,  
2,2,5,5-tetramethylcyclopentanol and  
1,1,3,3-tetramethylol-2-decalone

also those having the structural formulae of IV or V namely, 2,2-dimethylolindanone or 4,4-dimethylol-2-oxazolidone.

These compounds can be used without significant adverse sensitometric effects in any effective concentration such as for example from about 5 percent to about 50 percent based upon the weight of the organic colloid in the layer.

By use of the term "tempering" it will be understood to mean imparting to a hydrophilic colloid by an addend or agent, a high degree of rigidity or structural toughness resembling well-known hardening characteristics achieved heretofore by chemical cross-linking agents. When added to hydrophilic colloids such as photographic silver halide colloid-containing elements to toughen the various colloids therein, the tempering agents disclosed herein unexpectedly provide a high degree of toughness to those colloids without adversely affecting the sensitometric characteristics as chemical cross-linking agents sometimes do.

While the compounds, disclosed herein to achieve the desirable and unexpected properties set forth, are generally classified as simple organic polyols, they include various cyclic compounds and they are distinguished from those poly-hydroxy type compounds such as glycerol or glycol whose previous disclosed use in photographic gelatin emulsions has been as plasticizers. Plasticizing or softening is virtually the opposite of the action of the polyols used in the practice of this invention since the former is a softening and the latter, rigidizing or tempering. By the use of the term "mushiness" as applied to colloid-layers herein, it will be understood to mean the physical property of softness as determined in the numerical values recorded by a weighted stylus drawn across said layers.

Accordingly, it is an object of this invention to provide improved light-sensitive emulsions, comprising a hydrophilic colloid, these emulsions exhibiting improved sensitometric properties such as covering power, decreased density loss on drying, and improved toughness, said improved toughness being achieved without adversely effecting the desired sensitometric characteristics of the emulsions.

It is another object to provide simple polyol compounds which, when added to silver halide emulsions containing covering power addenda, toughen and temper said emulsions while still maintaining effective covering power.

It is still another object of this invention to provide novel colloidal compositions such as improved colloidal emulsions and the various photographic elements utilizing them.

It is yet another object to provide processes for imparting improved physical and chemical characteristics to



washed, e.g. by the procedures described in Hewitson et al. U.S. Pat. 2,618,556 issued Nov. 18, 1952; Yutzy et al. U.S. Pat. 2,614,928 issued Oct. 21, 1952; Yackel U.S. Pat. 2,565,418 issued Aug. 21, 1951; Hart et al. U.S. Pat. 3,241,969 issued Mar. 22, 1966; and Waller et al. U.S. Pat. 2,489,341 issued Nov. 29, 1949.

The emulsions used with this invention can be sensitized with chemical sensitizers, such as with reducing agents; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Suitable procedures are described in Sheppard et al. U.S. Pat. 1,623,499 issued Apr. 5, 1927; Waller et al. U.S. Pat. 2,399,083 issued Apr. 23, 1946; McVeigh U.S. Pat. 3,297,447 issued Jan. 10, 1967; and Dunn U.S. Pat. 3,297,446 issued Jan. 10, 1967.

The silver halide emulsions used with this invention can contain speed increasing compounds such as polyalkylene glycols, cationic surface active agents and thioethers or combinations of these as described in Piper U.S. Pat. 2,886,437 issued May 12, 1959; Dann et al. U.S. Pat. 3,046,134 issued July 24, 1962; Carroll et al. U.S. Pat. 2,944,900 issued July 12, 1960; and Goffe U.S. Pat. 3,294,540 issued Dec. 27, 1966.

The silver halide emulsions used in the practice of this invention can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers each used alone or in combination include thiazolium salts described in Brooker et al. U.S. Pat. 2,131,038 issued Sept. 27, 1938, and Allen et al. U.S. Pat. 2,694,716 issued Nov. 16, 1954; the azaindenes described in Piper U.S. Pat. 2,886,437 issued May 12, 1959; and Heimbach et al. U.S. Pat. 2,444,605 issued July 6, 1948; the mercury salts as described in Allen et al. U.S. Pat. 2,728,663 issued Dec. 27, 1955; the urazoles described in Anderson et al. U.S. Pat. 3,287,135 issued Nov. 22, 1966; the sulfo-catechols described in Kennard et al. U.S. Pat. 3,236,652 issued Feb. 22, 1966; the oximes described in Carroll et al. British Pat. 623,448 issued May 18, 1949; nitron; nitroindazoles; the mercaptotetrazoles described in Kendall et al. U.S. Pat. 2,403,927 issued July 16, 1946; Kennard et al. U.S. Pat. 3,266,897 issued Aug. 16, 1966, and Luckey et al. U.S. Pat. 3,397,987 issued Aug. 20, 1968; the polyvalent metal salts described in Jones U.S. Pat. 2,839,405 issued June 17, 1958; the thiuronium salts described in Herz et al. U.S. Pat. 3,220,839 issued Nov. 30, 1965; the palladium, platinum and gold salts described in Trivelli et al. U.S. Pat. 2,566,263 issued Aug. 28, 1951, and Yutzy et al. U.S. Pat. 2,597,915 issued May 27, 1952.

The photographic elements of this invention can contain incorporated developing agents such as hydroquinones, catechols, aminophenols, 3-pyrazolidones, ascorbic acid and its derivatives, reductones and phenylenediamines. Combinations of developing agents can be employed in the practice of the invention. The developing agents can be in a silver halide emulsion and/or in another suitable location in the photographic element. The developing agents can be added from suitable solvents or in the form of dispersions as described in Yackel U.S. Pat. 2,592,368 issued Apr. 8, 1952 and Dunn et al., French Pat. 1,505,778.

The photographic and other hardenable layers used in the practice of this invention can be hardened by various organic or inorganic hardeners, alone or in combination, such as the aldehydes, and blocked aldehydes, ketones, carboxylic and carbonic acid derivatives, sulfonate esters sulfonyl halides and vinyl sulfonyl ethers, active halogen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodiimides, mixed function hardeners and polymeric hardeners such as oxidized polysaccharides like dialdehyde starch and oxyguar gum and the like.

The photographic emulsions and elements described in the practice of this invention can contain various colloids alone or in combination as vehicles, binding agents and various layers. Suitable hydrophilic materials include both naturally-occurring substances such as proteins, for exam-

ple, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water soluble polyvinyl compounds like poly(vinylpyrrolidone), acrylamide polymers and the like.

The described photographic emulsion layers and other layers of a photographic element employed in the practice of this invention can also contain alone or in combination with hydrophilic, water permeable colloids, other synthetic polymeric compounds such as dispersed vinyl compounds such as in latex form and particularly those which increase the dimensional stability of the photographic materials. Suitable synthetic polymers include those described, for example, in Nottorf U.S. Pat. 3,142,568 issued July 28, 1964; White U.S. Pat. 3,193,386 issued July 6, 1965; Houck et al. U.S. Pat. 3,062,674 issued Nov. 6, 1962; Houck et al. U.S. Pat. 3,220,844 issued Nov. 30, 1965; Ream et al. U.S. Pat. 3,287,289 issued Nov. 22, 1966; and Dykstra U.S. Pat. 3,411,911 issued Nov. 19, 1968; particularly effective are those water-insoluble polymers of alkyl acrylates and methylacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, those which have crosslinking sites which facilitate hardening or curing, those having recurring sulfobetaine units as described in Dykstra Canadian Pat. 774,054.

The photographic elements used with this invention can contain antistatic or conducting layers, such layers can comprise soluble salts, e.g. chlorides, nitrates, etc., evaporated metal layers, ionic polymers such as those described in Minsk U.S. Pat. 2,861,056 issued Nov. 18, 1958 and Sterman et al., U.S. Pat. 3,206,312 issued Sept. 14, 1965 or insoluble inorganic salts such as those described in Trevoy U.S. Pat. 3,428,451 issued Feb. 18, 1969.

In addition, the photographic layers and other layers of a photographic element employed and described herein can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related films or resinous materials, as well as glass, paper, metal and the like. Typically, a flexible support is employed, especially a paper support, which can be partially acetylated or coated with baryta and/or an alphaolefin polymer, particularly a polymer of an alpha-olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylenebutene copolymers and the like.

The photographic layers employed in the practice of this invention can contain plasticizers and lubricants such as polyalcohols, e.g. glycerin and diols of the type described in Milton et al., U.S. Pat. 2,960,404 issued Nov. 1, 1966; fatty acids or esters such as those described in Robijns U.S. Pat. 2,588,765 issued Apr. 11, 1952, and Duane U.S. Pat. 3,121,060 issued Feb. 11, 1964; and silicone resins such as those described in Du Pont British Pat. 955,061 issued Apr. 15, 1964.

The photographic layers employed in the practice of this invention can contain surfactants such as saponin; anionic compounds such as the alkyl aryl sulfonates described in Baldsiefen U.S. Pat. 2,600,831 issued June 17, 1952; amphoteric compounds such as those described in Ben-Ezra U.S. Pat. 3,133,816 issued May 19, 1964; and water soluble adducts of glycidol and an alkyl phenol such as those described in Olin Mathieson British Pat. 1,022,878 issued Mar. 16, 1966.

The photographic elements employed in the practice of this invention can contain matting agents such as starch, titanium dioxide, zinc oxide, silica, polymeric beads including beads of the type described in Jelley et al., U.S. Pat. 2,992,101 issued July 11, 1961 and Lynn U.S. Pat. 2,701,245, issued Feb. 1, 1955.

The photographic elements used in this invention can contain brightening agents including stilbenes, triazines, oxazoles and coumarin brightening agents. Water soluble brightening agents can be used such as those described in Alberz et al., German Pat. 972,067 and McFall et al. U.S.

Pat. 2,933,390 issued Apr. 19, 1960 or dispersions of brighteners may be used such as those described in Jansen German Pat. 1,150,274, Oetiker et al., U.S. Pat. 3,406,070 issued Oct. 15, 1968 and Heidke French Pat. 1,530,244.

Spectral sensitizing dyes can be used conveniently to confer additional sensitivity to the light sensitive silver halide emulsion of the multilayer photographic elements of the invention. For instance, additional spectral sensitization can be obtained by treating the emulsion with a solution of a sensitizing dye in an organic solvent or the dye can be added in the form of a dispersion as described in Owens et al. British Pat. 1,154,781 issued June 11, 1969. For optimum results, the dye is either added to the emulsion as a final step or at some earlier stage.

Sensitizing dyes useful in sensitizing such emulsions are described, for example, in Brooker et al. U.S. Pat. 2,526,632 issued Oct. 24, 1950; Sprague U.S. Pat. 2,503,776 issued Apr. 11, 1950; Brooker et al. U.S. Pat. 2,493,748 issued Jan. 10, 1950; and Taber et al. U.S. Pat. 3,384,486 issued May 21, 1968. Spectral sensitizers which can be used include the cyanines, merocyanines, complex (tri or tetranuclear) merocyanines, complex (tri- or tetranuclear) cyanines, holopolar cyanines, styryls, hemicyanines (e.g. enamine hemicyanines), oxonols and hemioxonols.

Dyes of the cyanine classes can contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazoles, thiazoles, selenazoles and imidazoles. Such nuclei can contain alkyl, alkylene, hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminoalkyl and enamine groups and can be fused to carboxylic or heterocyclic ring systems either unsubstituted or substituted with halogen, phenyl, alkyl, haloalkyl, cyano, or alkoxy groups. The dyes can be symmetrical or unsymmetrical and can contain alkyl, phenyl, enamine or heterocyclic substituents on the methine or polymethine chain.

The merocyanine dyes can contain the basic nuclei mentioned above as well as acid nuclei such as thiohydantoin, rhodaniones, oxazolidenediones, thiazolidenediones, barbituric acids, thiazolineones, and malononitrile. These acid nuclei can be substituted with alkyl, alkylene, phenyl, carboxyalkyl, sulfoalkyl, hydroxyalkyl, alkoxyalkyl, alkylamino groups, or heterocyclic nuclei. Combinations of these dyes can be used, if desired. In addition, supersensitizing addenda which do not absorb visible light can be included, for instance, ascorbic acid derivatives, azaindenes, cadmium salts, and organic sulfonic acids as described in McFall et al. U.S. Pat. 2,933,390 issued Apr. 19, 1960, and Jones et al. U.S. Pat. 2,937,089 issued May 17, 1960.

The various layers, including the photographic layers, employed in the practice of this invention can contain light absorbing materials and filter dyes such as those described in Sawdey U.S. Pat. 3,253,921 issued May 31, 1966; Gaspar U.S. Pat. 2,274,782 issued Mar. 3, 1942; Silberstein et al. U.S. Pat. 2,527,583 issued Oct. 31, 1950, and VanCampen U.S. Pat. 2,956,879 issued Oct. 18, 1960. If desired, the dyes can be mordanted, for example, as described in Milton et al. U.S. Pat. 3,282,699 issued Nov. 1, 1966.

The sensitizing dyes and other addenda used in the practice of this invention can be added from water solutions or suitable organic solvent solutions can be used. The compounds can be added using various procedures including those described in Collins et al. U.S. Pat. 2,912,343 issued Nov. 10, 1959; McCrossen et al., U.S. Pat. 3,342,605 issued Sept. 19, 1967; Audran U.S. Pat. 2,996,287 issued Aug. 15, 1961 and Johnson et al., U.S. Pat. 3,425,835 issued Feb. 14, 1969.

The photographic layers used in the practice of this invention can be coated by various coating procedures including dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in Beguin U.S. Pat. 2,681,294 issued June 15, 1954. If

desired, two or more layers may be coated simultaneously by the procedures described in Russell U.S. Pat. 2,761,791 issued Sept. 4, 1956 and Wynn British Pat. 837,095. This invention also can be used for silver halide layers coated by vacuum evaporation as described in British Pat. 968,453 and LuValle et al. U.S. Pat. 3,219,451 issued Nov. 23, 1965.

This invention can be used with elements designed for color photography, for example, elements containing color-forming couplers such as those described in Frohlich et al. U.S. Pat. 2,376,679 issued May 22, 1945; Jelley et al., U.S. Pat. 2,322,027 issued June 15, 1943; Fierke et al., U.S. Pat. 2,801,171 issued July 30, 1957; Godowsky U.S. Pat. 2,698,794 issued Jan. 4, 1955; Barr et al., U.S. Pat. 3,227,554 issued Jan. 4, 1966; and Graham et al. U.S. Pat. 3,046,129 issued July 24, 1962; or elements to be developed in solutions containing color-forming couplers such as those described in Mannes et al. U.S. Pat. 2,252,718 issued Aug. 19, 1941; Carroll et al., U.S. Pat. 2,592,243 issued Apr. 18, 1952; and Schwan et al., U.S. Pat. 2,950,970 issued Aug. 30, 1966; and in false-sensitized color materials such as those described in Hanson U.S. Pat. 2,763,549 issued Sept. 18, 1956.

Photographic elements prepared according to this invention can be processed by various methods including processing in alkaline solutions containing conventional developing agents such as hydroquinones, catechols, aminophenols, 3-pyrazolidones, phenylenediamines, ascorbic acid derivatives, hydroxylamines, hydrazines, reductones and the like; web processing such as described in Tregillus et al. U.S. Pat. 3,179,517 issued Apr. 20, 1965; stabilization processing as described in Russell et al. "Stabilization Processing of Films and Papers," PSA Journal, vol. 16B, August 1950; monobath processing as described in Levy "Combined Development and Fixation of Photographic Images with Monobaths," Phot. Sci. and Eng., vol. 2, No. 3, October 1958, and Barnes et al. U.S. Pat. 3,392,019 issued July 9, 1968. If desired, the photographic elements of this invention can be processed in hardening developers such as those described in Allen et al., U.S. Pat. 3,232,761 issued Feb. 1, 1966; in roller transport processors such as those described in Russell et al., U.S. Pat. 3,025,779 issued Mar. 20, 1962; or by surface application processing as described in Example 3 of Kitze U.S. Pat. 3,418,132 issued Dec. 24, 1968.

The silver halide emulsions used with this invention can be used for making lithographic printing plates such as by the colloid transfer of undeveloped and unhardened areas of an exposed and developed emulsion to a suitable support as described in Clark et al. U.S. Pat. 2,763,553 issued Sept. 18, 1956; to provide a relief image as described in Woodward U.S. Pat. 3,402,045 issued Sept. 17, 1968 or Spencer U.S. Pat. 3,053,658 issued Sept. 11, 1962; to prepare a relief printing plate as described in Baxter et al. U.S. Pat. 3,271,150 issued Sept. 6, 1966.

This invention can be used with elements designed for colloid transfer processes such as described in Yutzky et al. U.S. Pat. 2,716,059 issued Aug. 23, 1953; silver salt diffusion transfer processes such as described in Rott U.S. Pat. 2,352,014 issued June 20, 1944; Land U.S. Pat. 2,543,181 issued Feb. 27, 1951; Yacket et al. U.S. Pat. 3,020,155 issued Feb. 6, 1962; and Land U.S. Pat. 2,861,885 issued Nov. 25, 1958; color image transfer processes such as described in Rogers U.S. Pat. 3,087,817 issued Apr. 30, 1963; 3,185,567 issued May 25, 1965; and 2,983,606 issued May 9, 1961; Weyerts et al. U.S. Pat. 3,253,915 issued May 31, 1966; Whitmore et al. U.S. Pat. 3,227,550 issued Jan. 4, 1966; Barr et al. U.S. Pat. 3,227,551 issued Jan. 4, 1966; Whitmore et al. U.S. Pat. 3,227,552 issued Jan. 4, 1966; and Land U.S. Pat. 3,415,644 issued Dec. 10, 1968; 3,415,645 issued Dec. 10, 1968; and 3,415,646 issued Dec. 10, 1968; and imbibition transfer processes as described in Minsk U.S. Pat. 2,882,156 issued Apr. 14, 1959.



Results obtained from the following examples indicate that known covering power addenda such as polyacrylamide and poly(vinyl  $\beta$  - hydroxyethylcarbonylmethylcarbamate), produce a marked softening or mushiness in photographic elements processed in both an automatic processor and the other known methods. These addenda also produce increased vertical swelling of the emulsion in water and a concomitant increase in mushiness of the gelatin layer. In contrast thereto, the polyol addenda useful in this invention in the same concentrations produce less mushiness and a significant increase in toughness and resistivity to deterioration of the physical integrity of the element. When these polyols are used in combination with the covering power addenda, substantial rigidity and toughness is noted by the decrease in percent vertical swell.

One test used to determine mushiness, i.e. lack of toughening, of the various colloid layers, involves the relative firmness or wet jelly strength of the various layers such as the gelatin emulsion layers or pelloid layers. These values are obtained based on a colloid-containing photographic element such as film or paper after removal from the processing solution, for example developer. The element is then drawn beneath a weighted stylus having a hard sapphire point on which the weighted force is varied, such as gradually increased to determine resistance. It is the force of this weight which causes a con-

means of the tempering polyols described and can be measured with accuracy.

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

## EXAMPLE I

In the example of the following tables, polyol tempering compounds are added and coated by known methods in the concentrations shown to a medium speed photographic silver bromiodide emulsion. The coatings of these examples are made on polyester (polyethylene terephthalate) support at 450 mg. silver/ft.<sup>2</sup> and 1248 mg. gel/ft.<sup>2</sup> for the medium speed silver bromiodide emulsion. The films are exposed to an Eastman IB sensitometer, developed in Kodak DK-50 Developer for 5 minutes, fixed, washed and dried.

The higher values recorded for mushiness indicate an increase in wet jelly strength and a reduced mushiness. The lower values recorded in percent vertical swell likewise indicate a general firming up and resistance to mushiness of the emulsion layer when the polyol compounds are added.

A further indication of the effective tempering achieved by the use of these polyols according to the practice of the present invention is shown by the improved toughness based on a reduced swell of the coatings after processing or immersion in high temperature baths.

TABLE I.—SILVER BROMIODIDE EMULSION

Addenda	Conc., g./m. Ag	One week incubation at 120° F. and 50% relative humidity											
		Fresh				Mushiness							Percent vertical swell distilled water
		Rel. speed	$\gamma$	Fog	Rel. speed	$\gamma$	Fog	Dev.	Fix	H <sub>2</sub> O			
Control		100	1.22	.02	204	1.08	.06	14	115	70	489		
N-[tris(hydroxymethyl)-methyl]hydroxyacetamide	50	107	1.22	.01	48	1.32	.05	18	122	76	359		
N-[tris(hydroxymethyl)-methyl]methoxyacetamide	50	110	1.24	.01	155	1.01	.53	26	141	102	345		
2,2,6,6-tetramethylolcyclohexanol	50	107	1.15	.01	316	1.05	.06	31	148	93	398		

NOTE.—All coatings contain 0.235% mucochloric acid based on the weight of gelatin in the emulsion layer plus a gelatin overcoat containing 0.34% mucochloric acid based on the weight of gelatin.

tinuous disruption or ploughing of the colloid layer surface, which is reported.

The numerical values recorded for determining mushiness will be higher in those instances where the emulsion or layer tested is firm and tempered in contrast to low values where mushiness appears and little resistance to the stylus is offered. Further, vertical swell is numerically determined by relative percent values and where the layer containing the addenda is suitably hardened, a lower figure appears indicating still less relative swelling in water or aqueous processing solutions. These values are obtained by well-known methods employing a swellometer.

In Table I, it can be seen that significant increases in toughness with concurrent loss of mushiness are reported for the compounds useful in the practice of the present invention.

The results set forth in all tables hereafter and obtained from the colloid-containing elements upon incubation are believed particularly significant since, at this time the effect of the chemical cross-linkage agents has substantially stabilized and the colloid strengthening is effected by

## EXAMPLE II

The following example shows that similar good results are obtained in the practice of the present invention in various types of silver halide compositions including, radiographic emulsions. In particular, the tempering polyols are added to various radiographic coarse-grain emulsions to provide toughness and rigidity to the colloid-containing layers. The coatings in the following table are made on polyester support at a coverage of 473 mg. silver/ft.<sup>2</sup> and 482 mg. gel./ft.<sup>2</sup>. As in Example I, these films are exposed to an Eastman 1B sensitometer, developed in Kodak DK-50 developer for 5 minutes, fixed, washed and dried. Similar good results are obtained when a high speed roller transport system is employed using the X-OMAT processor (a trademark of the Eastman Kodak Company for its high speed roller transport type processor). In obtaining those values, the developer solutions contain glutaraldehyde, a chemical crosslinking type hardener as described more fully in Belgian Pat. 700,301 of Barnes et al issued Aug. 31, 1967.

TABLE II.—RADIOGRAPHIC EMULSION  
(Fresh values)

Addenda:	Concentration grams/ mole Ag	X-Omat Processor, mushiness			Kodak DK-50 Developer, mushiness			Percent vertical swell distilled water
		Dev.	Fix	H <sub>2</sub> O	Dev.	Fix	H <sub>2</sub> O	
Polyacrylamide.....	20	28	28	28	12	38	26	457
Poly(vinyl $\beta$ -hydroxyethylcarbamylmethylcarbamate).....	20	28	31	34	18	43	33	450
2-(2-hydroxyethylamino)-2-(hydroxymethyl)-1,3-propanediol.....	{10	29	36	42	16	49	41	377
	20	49	57	60	31	62	52	238
2-[bis(2-hydroxyethyl)amino-2-hydroxymethyl]-1,3-propanediol.....	{10	46	58	57	26	66	52	373
	20	46	61	60	30	68	53	271
Control.....		30	47	46	10	50	46	385

NOTES:  
1. From the above it can be easily seen that by adding polyols in as little as one half of the concentration of the covering powering addenda used, significant increases in wet jelly strength as well as reduced mushiness and vertical swell in water are obtained.  
2. From the following results it can be seen that both reduced vertical swell and significant improvement in tempering evidenced by decreased mushiness values by various combinations of polyol and covering power addenda are achieved.

Polyacrylamide.....	20	28	28	28	12	38	26	457
Polyacrylamide and 2-(2-hydroxyethylamino)-2-(hydroxymethyl)-1,3-propanediol.....	{10 of each	26	32	32	11	57	36	378
	{20 of each	22	24	20	12	43	36	311
Poly(vinyl $\beta$ -hydroxyethylcarbamylmethylcarbamate).....	20	28	31	34	18	43	33	450
Poly(vinyl $\beta$ -hydroxyethylcarbamylmethylcarbamate) and 2-(2-hydroxyethylamino)-2-(hydroxymethyl)-1,3-propanediol.....	{10	18	31	34	9	38	31	387
	{20 of each	28	33	39	36	45	40	294

## EXAMPLE III

In order to demonstrate the effective strengthening of the all-gelatin system contained in the photographic element obtained by adding the tempering polyols described in the present invention, a procedure substantially as described in Example I is employed with the following results:

## EXAMPLE IV

Similar good toughening results are obtained in gelatin-latex systems in which these colloid combinations are tempered by the representative polyols of the group described herein. The photographic silver bromide emulsions are as described in Example I both as to coating and processing.

TABLE III.—SILVER BROMIODIDE EMULSION<sup>1</sup>

Addenda	Conc., g./m. Ag	Fresh			1 wk. incubation 120° F/50% RH			Fresh mushiness		
		Rel. speed	$\gamma$	Fog	Rel. speed	$\gamma$	Fog	Dev.	Fix	H <sub>2</sub> O
Control.....		100	1.13	.05	214	1.06	.09	8	99	63
Poly(acrylamide).....	50	112	1.21	.06	234	1.12	.08	4	38	38
Poly(acrylamide) plus	50	204	1.17	.09	417	1.04	.14	12	51	44
2-(2-hydroxyethylamino)-2-(hydroxymethyl)-1,3-propanediol.....	25									
Poly(vinyl $\beta$ -hydroxyethylcarbamylmethylcarbamate).....	50	118	1.27	.08	282	1.17	.07	9	53	51
Poly(vinyl $\beta$ -hydroxyethylcarbamylmethylcarbamate) plus	50	219	1.20	.09	436	0.98	.24	15	52	46
2-(2-hydroxyethylamino)-2-(hydroxymethyl)-1,3-propanediol.....	25									

<sup>1</sup> All coatings contain mucochloric acid at 0.235% as a hardener based on the weight of gelatin in the emulsion layer plus a gelatin overcoat containing 0.34% mucochloric acid based on the weight of gelatin.

TABLE IV.—GELATIN-LATEX<sup>1</sup>

Addenda	Conc., g./m. Ag	Fresh			1 wk. incubation 120° F/50% RH			Fresh mushiness		
		Rel. speed	$\gamma$	Fog	Rel. speed	$\gamma$	Fog	Dev.	Fix	H <sub>2</sub> O
Control.....		100	1.08	.06	204	1.05	.06	18	98	77
Polb(acrylamide).....	50	112	1.24	.06	191	1.19	.07	8	29	26
Polb(vinyl $\beta$ -hydroxyethylcarbamylmethylcarbamate).....	50	126	1.21	.06	263	1.18	.07	12	36	20
Polb(acrylamide) plus	50	191	1.18	.06	389	1.03	.11	23	44	49
2-(2-hydroxyethylamino)-2-(hydroxymethyl)-1,3-propanediol.....	25									
Poly(vinyl $\beta$ -hydroxyethylcarbamylmethylcarbamate).....	50	193	1.12	.07	398	0.99	.16	30	60	51
2-(2-hydroxyethylamino)-2-(hydroxymethyl)-1,3-propanediol.....	25									

<sup>1</sup> 2:1 gelatin-latex (copoly[methyl acrylate-3-acryloyloxypropylsulfonic acid, sodium salt -2-acetoacetoxyethyl methacrylate]).

NOTE.—All coatings contain mucochloric acid at 235% based on the weight of gelatin in the emulsion layer plus a gelatin percoat containing 0.34% mucochloric acid based on the weight of gelatin.

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EXAMPLE V

The results set forth in the following tables show that substantial rigidity and toughness is imparted by the polyols representative of the group described in this invention to various emulsions such as those photographic emulsions to which covering power addenda are likewise added. The coating and processing of the photographic emulsions are the same as those previously described in Example I.

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EXAMPLE VI

Several photographic elements are prepared by coating a light-sensitive composition comprising a medium speed silver bromiodide photographic emulsion at a coverage of 450 mg./silver/ft.<sup>2</sup> in gelatin binder at a coverage of 1248 mg./ft.<sup>2</sup> on a polyethylene terephthalate film support. These films are exposed on an Eastman 1B sensitometer, developed in Kodak DK-50 developer, i.e. an elon-hydroquinone containing developer, for 5 minutes,

TABLE V.—SILVER BROMIODIDE EMULSION<sup>1</sup>

Addenda	Conc., g./m. Ag	Fresh		1 wk. incubation, 120° F./50% RH			Fresh, mushiness		Mushiness in developer		
		Rel. speed	$\gamma$	Fog	Rel. speed	$\gamma$	Fog	Fix	H <sub>2</sub> O	Fresh	Incuba- tion
Control.....		100	1.24	.02	214	1.11	.08	117	86	6	14
Poly(acrylamide).....	50	115	1.30	.02	200	1.19	.08	47	51	6	12
Poly(vinyl $\beta$ -hydroxyethylcarbamylmethylcarbamate).....	50	120	1.32	.02	251	1.19	.07	70	79	13	13
2-(2-hydroxyethylamino)-2-(hydroxymethyl)-1,3-propanediol.....	50	178	1.18	.02				148	108	6	25
2-[bis(2-hydroxyethyl)amino]-2-(hydroxymethyl)-1,3-propanediol.....	50	174	1.15	.01	295	1.02	.12	144	90	5	23
Polyacrylamide.....	50										
and 2-(2-hydroxyethylamino)-2-(hydroxymethyl)-1,3-propanediol.....	30	178	1.27	.01	339	1.04	.11	70	67	20	14
Polyacrylamide.....	50										
and 2-[bis(2-hydroxyethyl)amino]-2-(hydroxymethyl)-1,3-propanediol.....	30	148	1.27	.01	276	1.09	.07	71	66	21	15
Poly(vinyl $\beta$ -hydroxyethylcarbamylmethylcarbamate).....	50										
and 2-(2-hydroxyethylamino)-2-(hydroxymethyl)-1,3-propanediol.....	30	186	1.32	.02	407	1.04	.24	86	75	24	20
Poly(vinyl $\beta$ -hydroxyethylcarbamylmethylcarbamate).....	50										
and 2-[bis(2-hydroxyethyl)amino]-2-(hydroxymethyl)-1,3-propanediol.....	30	162	1.30	.02	302	1.14	.08	82	64	20	18

NOTE.—All coatings contain mucochloric acid at 0.235% based on the weight of gelatin in the emulsion layer plus a gelatin overcoat containing 0.34% mucochloric acid based on the weight of gelatin.

followed by fixing, washing and drying. Sensitometric data and physical measurements are recorded as follows:

TABLE VI-A.—SILVER BROMIODIDE EMULSION<sup>1</sup>

Addenda	Conc., g./m. Ag	Fresh			1 wk. incubation, 120° F./50% RH			Mushiness			Fresh, percent vertical swell dist. water
		Rel. speed	$\gamma$	Fog	Rel. speed	$\gamma$	Fog	Developer, fresh/ incubation	Fix	H <sub>2</sub> O	
Control.....		100	1.10	.09	219	1.04	.06	18/36	111	80	398
Poly(acrylamide).....	50	107	1.18	.08	191	1.07	.06	12/22	56	59	412
N-[tris(hydroxymethyl)methyl]-o-methoxybenzamide.....	50	107	1.09	.07	246	1.06	.06	12/34	95	80	418
2-acrylamido-2-hydroxymethyl-1,3-propanediol.....	50	89	1.06	.07	191	1.00	.06	21/60	118	79	346
2,2,6,6-tetramethylolethylcyclohexanol.....	50	118	1.10	.07	389	1.00	.06	28/64	112	90	318
Trimethylolethane.....	50	105	1.02	.07	339	.98	.06	36/78	125	94	287
Poly(acrylamide).....	50										
and 2,2,6,6-tetramethylolethylcyclohexanol.....	25	105	1.20	.08	200	1.08	.06	9/20	46	53	418
Poly(acrylamide).....	50										
and 1,3-propanediol.....	25	105	1.19	.07	178	1.08	.06	12/25	57	50	400
Poly(acrylamide).....	50										
and methyl-o-methoxybenzamide.....	25	118	1.18	.07	234	1.05	.06	8/19	50	42	435
Poly(acrylamide).....	50										
and Trimethylolethane.....	25	115	1.16	.07	219	1.11	.06	15/30	65	65	369

<sup>1</sup> All coatings contain mucochloric acid at 0.235% based on the weight of gelatin in the emulsion layer plus a gelatin overcoat containing 0.34% mucochloric acid based on the weight of gelatin.

TABLE VI-B.—SILVER BROMIODIDE EMULSION<sup>1</sup>

Addenda	Conc., g./m. Ag	Fresh			Mushiness			Percent vertical swell dist. water
		Rel. speed	$\gamma$	Fog	Dev.	Fix	H <sub>2</sub> O	
Control.....		100	1.14	.01	42	156	86	391
2-(2-hydroxyethylamino)-2-(hydroxymethyl)-1,3-propanediol.....	25	151	1.09	.01	48	175	130	404
Do.....	50	219	1.00	.01	71	200	150	313
2-[bis(2-hydroxyethyl)amino]-2-(hydroxymethyl)-1,3-propanediol.....	25	118	1.11	.01	46	172	129	369
Do.....	50	151	1.11	.01	58	187	136	311
Butyl tri(hydroxymethyl)acetate.....	50	85	1.12	.01	39	172	118	293
1,6-hexanediamine di[tris(hydroxymethyl)acetic acid addition salt].....	20	148	1.12	.01	7	100	74	462
Tris(hydroxymethyl)methylamine glycolic acid addition salt.....	25	91	1.16	.01	30	155	107	413
Do.....	50	82	1.22	.01	32	148	120	328

<sup>1</sup> All of the coatings contained 0.235% mucochloric acid based on the weight of gelatin in the emulsion layer plus a gelatin overcoat containing 0.34% mucochloric acid based on the weight of gelatin.

The tougheners in accordance with our invention have shown themselves to be useful in color photography such as in photographic emulsions in which color couplers have been incorporated. The use of these polyols results in layer toughness with little adverse sensitometric effects used in levels producing satisfactory tempering in contrast with some of the crosslinking types of gelatin hardeners. No adverse effects upon dye hue or stability of the emulsion has been observed. For instance, in a photographic product in which coatings of the following structure were applied to a support these tempering agents have been used with good effect:

Layer 6—Gelatin layer.

Layer 5—Red-sensitive silver chlorobromide gelatin consisting of 90 mole percent bromide and a phenolic cyan coupler of the type described in U.S. Pat. 2,423,730, issued to Salminin et al., on July 8, 1947.

Layer 4—Gelatin layer and an ultraviolet absorber.

Layer 3—Green-sensitive silver chlorobromide gelatin emulsion consisting of 80 mole percent chloride and a pyrazolone magenta coupler of the types described in U.S. Pat. 2,600,788, issued to Loria et al., on June 17, 1952.

Layer 2—Gelatin layer.

Layer 1—Blue-sensitive silver chlorobromide gelatin emulsion consisting of 98 mole percent bromide and an acyl acetanilide yellow coupler of the type described in U.S. Pat. 2,875,057, issued to McCrossen et al., on Feb. 24, 1959.

The polyols in accordance with our invention can be used in all six of the layers of the product or they can be used in the emulsion compositions with other hardeners being used in the gelatin layers if desired.

#### EXAMPLE VII

In a manner similar to that described in the foregoing example, additional photographic examples are prepared

by coating onto a polyethylene terephthalate film support a coarse grain silver bromide gelatin emulsion having 6 mole percent iodide and the remainder, bromide. Silver bromide covering is effected at 459 mg. silver per square foot and gelatin coverage at 1037 mg. per square foot. The following stable records various swell measurements and demonstrates that the toughening compounds useful in the practice of the present invention appear to differ in their mechanism of action when compared to known crosslinking compounds, the latter exhibiting a swell value of substantially less than 500%.

TABLE VII

Compound present	Percent	
	Concentration <sup>1</sup>	Swell
Control.....		640
Mucochloric acid.....	0.5	410
Formaldehyde.....	0.5	320
Bis(vinylsulfonylmethyl) ether.....	1.0	310
Do.....	3.0	220
Do.....	6.0	190
2,2,6,6-tetramethylol cyclohexanol.....	1.0	650
Do.....	3.0	640
Do.....	6.0	640
4,4-dimethyloloxazolidone.....	6.0	630
2,2,5,5-tetramethylol cyclopentanone.....	1.0	680
Do.....	3.0	700
Do.....	6.0	660
2,2-dimethollindanone.....	1.0	640
Do.....	3.0	590
Do.....	6.0	550

<sup>1</sup> Concentration described as percent compound by weight present per total weight of gelatin.

#### EXAMPLE VIII

As in Example VI, still other photographic examples are prepared in the same manner as described. Tables VIII-A and VIII-B which follow record the fresh and incubated sensitometric values along with the corresponding mushiness in various processing solutions. The percent swell determined in fresh examples and after incubation, clearly demonstrates the superior properties of the compounds useful in the practice of this invention.

TABLE VIII-A

Compound present	Level (g./Ag mole)	Fresh			1 wk. 120°/50% relative humidity (incubation)			Mushiness (fresh/incubation)			Percent swell (fresh/incubation)
		Rel. speed	$\gamma$	Fog	Rel. speed	$\gamma$	Fog	Dev.	Fix	Wash	
Control.....		100	1.18	0.09	191	1.11	0.08	10/24	96/138	67/99	540/367
4,4-bis(hydroxymethyl)-2-oxazolone.....	50	97	1.17	0.07	282	1.09	0.08	17/56	104/200+	90/154	443/278
Poly(acrylamide).....	50	105	1.30	0.08	204	1.13	0.08	5/12	41/49	46/48	552/403
2,2,6,6-tetramethylol cyclohexanol.....	25	112	1.12	0.07	251	1.11	0.08	16/35	120/148	88/112	468/355
2,2,6,6-tetramethylol cyclohexanol.....	50	110	1.13	0.06	295	1.11	0.08	21/47	128/134	101/131	436/314
2,2,6,6-tetramethylol cyclohexanol..... plus	25										
Polyacrylamide.....	25	107	1.17	0.07	257	1.11	0.07	12/23	76/98	70/82	490/373

NOTE.—All coatings contain 0.235% mucochloric acid based on the weight of gelatin in the emulsion layer plus a gelatin overcoat containing 0.34% mucochloric acid based on the weight of gelatin.

TABLE VIII-B

Compound present	Level (g./Ag mole)	Fresh			1 wk. 120°/50% relative humidity (incubation)			Mushiness (fresh/incubation)			Percent swell (fresh/incubation)
		Rel. speed	$\gamma$	Fog	Rel. speed	$\gamma$	Fog	Dev.	Fix	Wash	
Control.....		100	1.02	0.06	118	1.01	0.06	18/32	92/123	68/86	500/309
Poly[2-acrylamidoethyltris(hydroxymethyl)acetate].....	18.8	87	1.10	0.06	100	1.09	0.06	14/24	62/80	56/64	528/356
2,2,5,5-tetramethylolcyclopentanone.....	25.0	170	0.88	0.10	159	0.93	0.07	16/43	114/138	52/94	443/289
2,2,5,5-tetrahydroxymethylcyclopentanone.....	40.8	155	0.91	0.06	112	0.98	0.07	20/40	112/138	58/102	442/291
2,2-dimethollindanone.....	25.0	141	0.93	0.05	148	1.01	0.05	34/52	136/158	70/108	378/273
Do.....	50.0	162	0.89	0.07	174	0.97	0.05	64/88	144/181	87/163	309/222
1,1,3,3-tetramethylol-2-decalone.....	25.0	110	0.84	0.06	132	0.88	0.08	54/77	152/157	96/116	229/175
Do.....	50.0	110	0.71	0.08	129	0.87	0.05	76/99	156/148	97/112	86/77
N,N'-[tris(hydroxymethyl)methyl]urea.....	21.2	209	1.00	0.03	195	1.00	0.07	12/23	100/124	62/91	495/333
N,N'-[tris(hydroxymethyl)methyl]urea..... plus	21.2										
Polyacrylamide.....	25.0	204	1.06	0.08	191	1.05	0.06	8/21	56/73	56/65	533/356
N-[tris(hydroxymethyl)methyl]tris(hydroxymethyl)acetamide.....	15.2										
Do..... plus	15.2	115	1.19	0.06	97	1.20	0.06	7/22	52/69	52/65	509/334
Polyacrylamide.....	25.0										

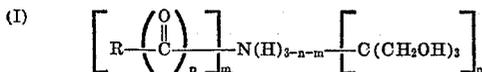
NOTE.—All coatings contain 0.235% mucochloric acid based on the weight of gelatin in the emulsion layer plus a gelatin overcoat containing 0.34% mucochloric acid based on the weight of gelatin.

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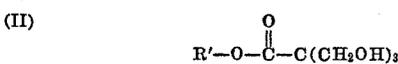
The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

There is claimed:

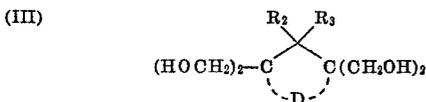
1. A photographic silver-halide element comprising a support, a hydrophilic colloid layer chemically hardened by reaction with a cross-linking agent and, in a concentration sufficient to temper said colloid, a tempering compound having the formula:



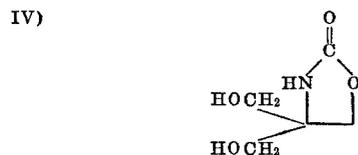
wherein R is phenyl or substituted phenyl selected from the group consisting of o-methoxyphenyl, 2,4-dichlorophenyl, p-tolyl, p-bromophenyl, 2,4-xylyl, p-acetylphenyl and p-biphenyl; alkyl group of from 1 to 8 carbon atoms; substituted alkyl selected from the group consisting of hydroxymethyl, methoxymethyl, hydroxyethyl, 3-chloropropyl and benzyl or alkenyl; p is 0 or 1; m is 0, 1 or 2; and n is 1 or 2; the sum of m and n being at most 3; or



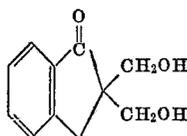
wherein R' is alkyl group of from 1 to 8 carbon atoms, a hydrogen atom, an alkali metal or the atoms necessary to complete an ammonium salt group; or



wherein D is the atoms needed to complete a 5 or 6 membered carbocyclic ring; and taken separately, R<sub>2</sub> is hydrogen and R<sub>3</sub> is hydroxy, or taken together R<sub>2</sub> with R<sub>3</sub> represents an oxo-group or



or  
(V)



said tempering compound is present in said element in admixture with said hydrophilic colloid in an amount equal to from about 5 to about 50 weight percent of said hydrophilic colloid.

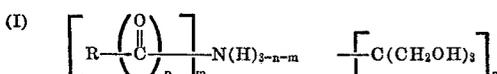
2. The element of claim 1 in which said tempering compound is present in combination with said silver halide or a layer adjacent thereto.

3. The element of claim 1 in which said silver halide is combined with the colloid to be tempered.

4. The element of claim 2 in which said silver halide is present as an emulsion layer.

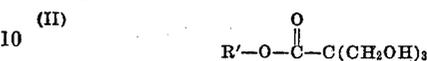
5. The element of claim 1 further comprising color-forming couplers.

6. A process for tempering a photographic silver halide element comprising a support, a hydrophilic colloid layer chemically hardened by reaction with a cross-linking agent which process comprises incorporating into said layer or in a layer adjacent thereto a tempering concentration of a compound having the structural formula:

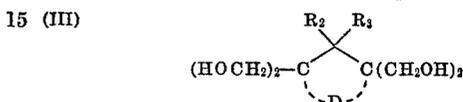


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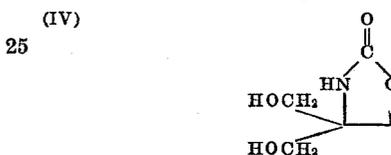
wherein R is phenyl, or substituted phenyl selected from the group consisting of o-methoxyphenyl, 2,4-dichlorophenyl, p-tolyl, p-bromophenyl, 2,4-xylyl, p-acetylphenyl, p-biphenyl; substituted alkyl selected from the group consisting of hydroxymethyl, methoxymethyl, hydroxyethyl, 3-chloropropyl and benzyl; or alkenyl; p is 0 or 1; m is 0, 1 or 2; and n is 1 or 2; the sum of m and n being at most 3; or



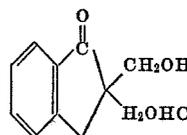
wherein R' is an alkyl group of from 1 to 8 carbon atoms, a hydrogen atom, an alkali metal or the atoms necessary to complete an ammonium salt group; or



wherein D is the atoms needed to complete a 5 or 6 membered carbocyclic ring; and taken separately R<sub>2</sub> is hydrogen and R<sub>3</sub> is hydroxy, or taken together R<sub>2</sub> and R<sub>3</sub> represents an oxo-group or



or  
(V)



said tempering concentration is in an amount equal to from about 5 to about 50 weight percent of said hydrophilic colloid.

7. The element of claim 1 in which said hydrophilic colloid is gelatin.

8. The element of claim 1 which further comprises a substantially dried latex resulting from the polymerization of a substantially water insoluble alkyl ester of an ethylenically unsaturated acid.

9. The element of claim 1 in which said tempering compound is:

2-(2-hydroxyethylamino)-2-(hydroxymethyl)-1,3-propanediol; or

2[bis(2-hydroxyethyl)amino]-2-(hydroxymethyl)-1,3-propanediol; or

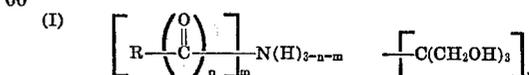
2,2,6,6-tetramethylolcyclohexanol; or

2,2,5,5-tetramethylolcyclopentanol; or

1,1,3,3-tetramethylol-2-decalone; or

2,2-dimethylolindanone.

10. A photographic silver halide hydrophilic chemically hardened colloid emulsion containing a tempering concentration of a compound having the structural formula:



wherein R is phenyl or substituted phenyl selected from the group consisting of o-methoxyphenyl, 2,4-dichlorophenyl, p-tolyl, p-bromophenyl, 2,4-xylyl, p-acetylphenyl, p-biphenyl; substituted alkyl selected from the group consisting of hydroxymethyl, methoxymethyl, hydroxyethyl, 3-chloropropyl and benzyl; or alkenyl; p is 0 or 1; m is 0, 1 or 2; and n is 1 or 2; the sum of m and n being at most 3; or

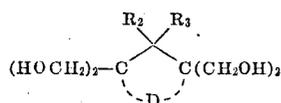


wherein R' is alkyl group of from 1 to 8 carbon atoms,

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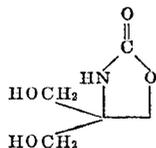
a hydrogen atom, an alkali metal or the atoms necessary to complete an ammonium salt group; or

(III)

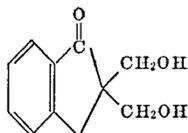


wherein D is the atoms needed to complete a 5 or 6 membered carbocyclic ring; and taken separately, R<sub>2</sub> is hydrogen and R<sub>3</sub> is hydroxy, or taken together R<sub>2</sub> with R<sub>3</sub> represents an oxo-group or

(IV)



or



11. The emulsion of claim 10 in which said hydrophilic colloid comprises gelatin.

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12. A layer derived from a chemically hardened and dried combination of a gelatin sol and a latex resulting from the polymerization of a substantially water-insoluble alkyl ester of an ethylenically unsaturated acid and containing coarse-grain silver halide; said latex and gelatin combination tempered by an effective tempering concentration of a compound having the formula of claim 1 said effective concentration is from about 5 to about 50 weight percent, based on the weight of hydrophilic colloid in said layer.

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U.S. Cl. X.R.

260-117; 106-125; 96-94

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