

[54] **SULFONATED POLY(VINYL ALCOHOL) DERIVATIVES AS ABSORBENT LAYERS IN PHOTOGRAPHIC PROCESSING WEBS**

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[52] U.S. Cl. 96/76, 96/114

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[58] Field of Search 96/29, 114, 76

[56] **References Cited**

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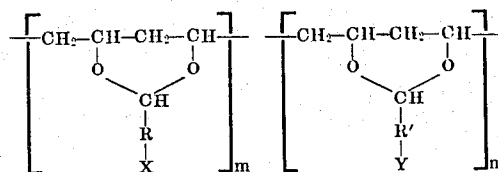
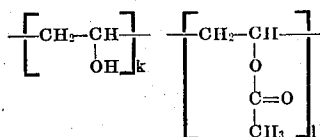
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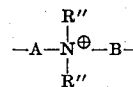
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[57] **ABSTRACT**

A photographic processing web comprising a support having an absorbent layer for alkaline photographic processing solutions, said layer comprising a cross-linked polymer product of a polymer composed of recurring segments having the structure:



wherein k indicates about 64 to 95 mole percent, l indicates about 0 to 15 mole percent, m indicates about 5 to 20 mole percent, n indicates about 0 to 10 mole percent; X is SO_3^- or $-\text{SO}_3^-Z$ wherein Z is an alkali metal or hydrogen; R' is an alkylamino group; Y is a radical containing an active methylene group and R is a phenylene group or the positively charged portion of an inner salt having the structure:



wherein A and B are alkylene groups and R'' is hydrogen or an alkyl group, with the proviso that when R is the positively charged portion of an inner salt, X is SO_3^- , said layer having incorporated therein a silver precipitating agent.

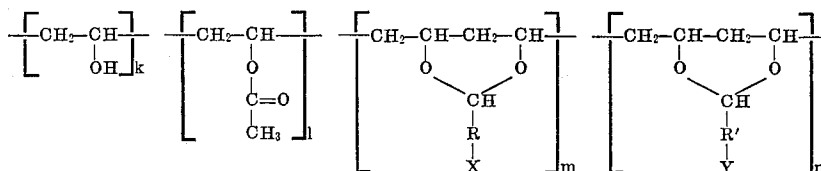
SULFONATED POLY(VINYL ALCOHOL) DERIVATIVES AS ABSORBENT LAYERS IN PHOTOGRAPHIC PROCESSING WEBS

FIELD OF THE INVENTION

This invention relates to photographic processing webs and particularly to improved, highly absorptive, hydrolysis-resistant vehicles for such processing webs.

DESCRIPTION OF THE PRIOR ART

It is well known to process photographic materials by surface application procedures in which the amount of



processing solution used is held at the minimum required for the development of the latent image, the removal of the residual silver or the like. Processing is thereby simplified and the size and complexity of the apparatus required is reduced.

One common form of surface application processing uses a web, or absorbent layer, containing processing solution which is maintained in contact with the exposed emulsion layer until processing is complete. Several webs may be used to apply a succession of processing solutions, or development and stabilization can be carried out simultaneously with a web imbibed with a monobath. In some cases, the residual silver halide is solubilized and caused to diffuse into the web to form a reversal positive image.

Gelatin has been used as a vehicle in processing webs. It is quite satisfactory when the web is stored in a dry state and wetted with processing solution shortly before use. However, because gelatin contains bonds susceptible to basic hydrolytic cleavage, the webs are subject to deterioration if they are presoaked and held for an appreciable time before use. This militates against the manufacture of presoaked webs and consequently imposes a serious inconvenience on the consumer. In an attempt to develop a stable presoaked web, many polymers have been tested including poly(vinyl alcohol), an 80:20 weight ratio copolymer of ethyl acrylate and acrylic acid, the carboxy ester resin lactone described in U.S. Pat. No. 3,007,901, and regenerated cellulose. These polymers failed for one or more of the following reasons: (1) inability to soak up and retain the imbiant; (2) physical weakness; (3) inability to be hardened; (4) chemical instability; (5) inhibition of physical development.

STATEMENT OF THE INVENTION

One object of the invention is to provide a photographic processing element or web having a hydrophilic absorbent layer for alkaline photographic processing solutions which is stable in hot water and in said processing solutions and which exhibits the property of high absorptivity.

Thus, it is an object of the invention to prepare highly absorptive photographic processing elements or webs which are stable during storage in the presence of alkaline processing solutions.

It is a further object of the invention to provide photographic processing webs having a hydrophilic absorbent layer comprising certain polymers containing sulfo-acetal groups cross-linked with a hardener.

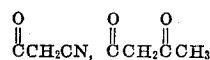
Another object of the invention is to provide a photographic processing web having a highly absorbent layer comprised of certain polymers containing sulfo-acetal groups and additionally active methylene groups which improve the ability to harden the coated web by cross-linking with a hardener.

Yet another object of the invention is to provide novel compositions characterized by an inner salt structure useful for the

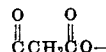
preparation of novel poly(vinyl acetals) which exhibit the properties of high absorptivity and stability to alkaline processing solutions and which are useful in photographic elements.

- These and other objects of the invention are obtained by providing webs which are either self-supporting layers or webs having at least one surface of a water-insensitive support with an absorbent layer for alkaline photographic processing solutions. The self-supported layer or layer on a support comprises a cross-linked polymer product of a polymer comprising 5 to 20 mole percent of vinyl sulfo-acetal units. In a preferred embodiment the polymer is composed of recurring segments having the structure:

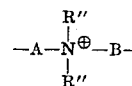
- wherein k indicates about 64 to 95 mole percent, l indicates about 0 to 15 mole percent, m indicates about 5 to 20 mole percent, n indicates about 0 to 10 mole percent; X is SO_3^- or $-\text{SO}_3\text{Z}$ wherein Z is an alkali metal or hydrogen such as sodium, potassium, and lithium; R' is an alkylamino group, e.g., $-(\text{CH}_2)_x-\text{NH}-$, wherein x equals 1 to 4 or more; Y is a radical containing an active methylene group such as



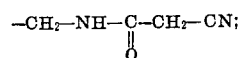
and



- lower alkyl of one to four carbon atoms; R is (1) a phenylene group which may be unsubstituted or substituted as, for instance, sulfophenylene (substituted with $-\text{SO}_3\text{Z}$ groups) and/or alkoxyphenylene such as methoxyphenylene (substituted with $-\text{OCH}_3$ groups) wherein Z is H or as defined above or (2) the positively charged portion of an inner salt having the structure:



- wherein A and B are alkylene groups, preferably of three to four carbon atoms and R'' is hydrogen or an alkyl group, preferably a lower alkyl group, with the proviso that when R is the positively charged portion of an inner salt, X is SO_3^- and the group $-\text{R}'\text{Y}$ is preferably



preferably the layer has incorporated therein a silver precipitating agent.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

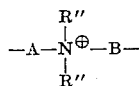
The polymers employed to form the absorbent layer of the photographic processing web of the invention wherein R in the general formula above is a phenylene group may be prepared by reacting benzene monoaldehydes containing as

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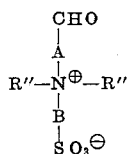
one or more substituents sulfonic acid groups or their corresponding alkali metal salts with polyvinyl alcohol.

Illustrative of sulfonic acid or salt group-substituted benzene monoaldehydes which may be used are ortho-, meta- or para-benzaldehyde sulfonic acids, 1-benzaldehyde-2,4-disulfonic acid, 1-benzaldehyde-2,5-disulfonic acid, 1-benzaldehyde-2,3-disulfonic acid, 4-methoxy-1-benzaldehyde-3-sulfonic acid and the like, and the corresponding sodium, potassium and lithium sulfonic acid salts of each of the above specified compounds. The preferred benzaldehyde reactants are the sodium sulfo benzaldehydes, particularly sodium 2,4-disulfo benzaldehyde.

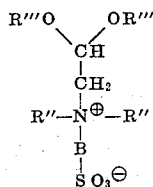
The polymers used in the formation of the absorbent layer of the invention wherein R in the general formula is the positively charged portion of an inner salt structure:



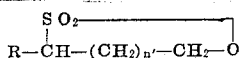
wherein A, B and R'' are as defined above, may be produced by reacting polyvinyl alcohol, polyvinyl acetate or partially hydrolyzed polyvinyl alcohol with an azonia sulfonate alkylaldehyde which can be represented by the general formula:



wherein A, B and R'' are as defined above. These azonia sulfonate alkylaldehydes are compounds which may be conveniently obtained from azonia sulfonate dialkyl acetals having the structure:



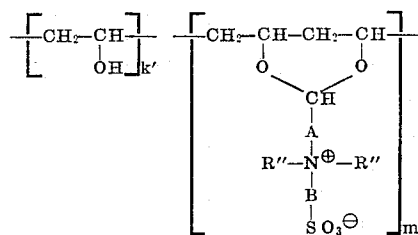
wherein R''' is an alkyl group, preferably a lower alkyl and R'' and B are as defined above, by hydrolysis under the acidic conditions. The azonia sulfonate dialkyl acetal compounds may be obtained by reacting an amino acetaldehyde dialkyl acetal with an alkyl sultone such as those having the structure:



wherein n' is 1 or 2 and R is hydrogen when n' is 1, or hydrogen or methyl when n' is 2, preferably in a suitable inert solvent reaction media such as acetonitrile. Illustrative of

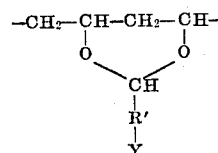
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in the art. The amino acetaldehyde dialkyl acetals may be used in the condensation reaction with the polyvinyl alcohols or polyvinyl acetates to form the polymers containing the inner salt structure since the condensation conditions employed hydrolyze in situ the acetal to the aldehyde derivative which then condenses with hydroxyl groups of the polyvinyl alcohol. In one embodiment, the cross-linked polymer product is of a polymer composed of recurring segments having the structure:



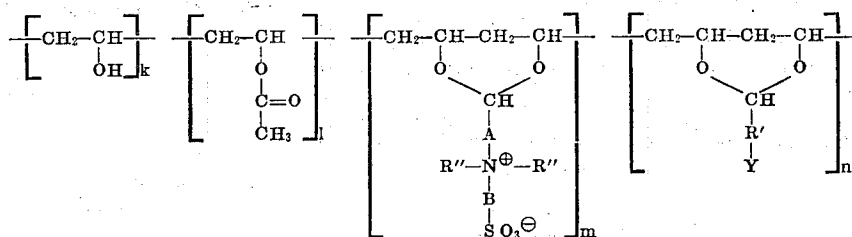
wherein k' indicates about 80 to 95 mole percent, m' indicates about 5 to 20 mole percent, and A, B and R'' are as defined above.

If desired and as can be seen from the general structures of the polymers of the invention, the useful polymers contain, in addition to the sulfo-acetal linkages, acetal linkages having a radical containing an active methylene group as represented by the following linkage:



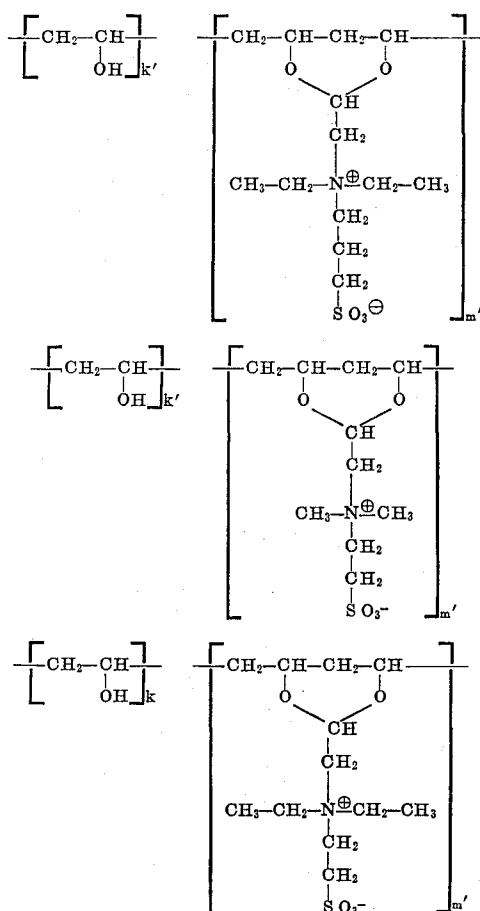
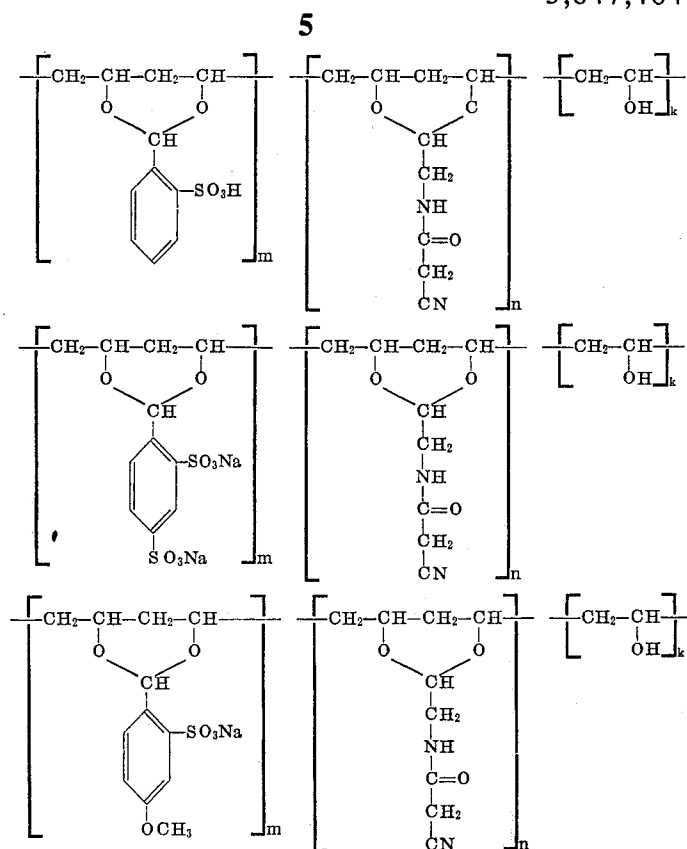
These linkages provide another reactive center which improves the hardening of the layers of the polymers when they are subsequently subjected to cross-linking as will be further described below. The active methylene-containing groups may be provided the polymers by, for instance, partially acetalizing polyvinyl alcohol or acetate with an aldehyde or acetal derivative of an active methylene group-containing compound. Preferred among the latter compounds are cyanoacetamino acetaldehyde dialkyl acetals such as cyanoacetamido acetaldehyde diethyl acetal. The partial acetalization with the active methylene-containing acetals or aldehydes may be accomplished either before or after introduction of sulfoacetal groups.

Reaction of the novel azonia sulfonate dialkyl acetal or aldehyde compounds with polyvinyl alcohol, polyvinyl acetate or partially hydrolyzed polyvinyl acetate provides novel polymers having the following structure;



suitable alkyl sultones are 1,3-propane sultone, 1,3-butane sultone and 1,4-butane sultone. Recovery of the azonia sulfonate dialkyl acetal product may be accomplished, for instance, by conventional crystallization techniques well known

wherein A, B, R', R'', Y, k , l , m and n are as defined above. The cross-linked polymer products of the invention include polymers composed of recurring segments having the structures below:



wherein in the above structures k , m , n , k' and m' , are as defined above.

- 40 The acetalization reaction may be effected by condensing the polyvinyl alcohol, polyvinyl acetate or partially hydrolyzed polyvinyl acetate and the aldehyde and acetal derivatives described above in the presence of a mineral acid such as phosphoric acid and in the manner described in German Pat. No. 643,650 and the working examples below. The extent of acetalization in all these cases may vary but in every instance the condensation should be carried out until about 5 to 20 mole percent of the vinyl alcohol and/or vinyl acetate groups have been acetalized to sulfo-acetal groups.

- 50 The polyvinyl alcohol, polyvinyl acetate or partially hydrolyzed polyvinyl acetate reactants employed may be of low, intermediate and high viscosity having a molecular weight generally in the range of 5,000 to 50,000.

- 55 The silver precipitating agents which can be incorporated in the absorbent layer of the processing webs may be physical development nuclei or chemical precipitants including (a) heavy metals, especially in colloidal form, and the salts of these metals (b) salts, the anions of which form a silver salt less soluble than the silver halide of the photographic emulsion to be processed, or (c) nondiffusing polymeric materials with functional groups capable of combining with and insolubilizing silver ion. Suitable silver precipitating agents for use in the invention are disclosed in Rott U.S. Pat. No. 2,352,014,

- 65 Yutzky and Yackel U.S. Pat. No. 2,740,717 and in Yackel et al. U.S. Pat. application Ser. No. 586,705 filed May 23, 1956, now U.S. Pat. No. 3,020,155 issued Feb. 6, 1962. More specifically, useful silver precipitating agents include sulfides, selenides, polysulfides, polyselenides, thiourea and its derivatives, mercaptans, stannous halides, silver, gold, platinum, palladium, and mercury, colloidal sulfur, aminoguanidine sulfate, aminoguanidine carbonate, arsenous oxide, sodium stannite, substituted hydrazines, xanthates, and the like. Polyvinyl mercaptoacetate is an example of a nondiffusing polymeric silver precipitant. Heavy metal sulfides such as lead, silver, zinc,

nickel, antimony, cadmium and bismuth sulfides are useful, particularly the sulfides of lead and zinc alone or in admixture, or complex salts of these with thioacetamide, dithio-oxamide or dithio-biuret. The heavy metals and the noble metals particularly in colloidal form are especially effective. Other silver precipitating agents will occur to those skilled in the art.

The concentrations of silver precipitants in the hydrophilic layer of the web must at least be sufficient to insure positive and complete removal of undeveloped silver halide from the light sensitive element to be processed. However, it has been found that a very considerable degree of control of the sensitometric properties of the image in web processed photographic material can be obtained through choice of the silver precipitant and by adjusting its concentration. For example, Carey-Lea silver nuclei incorporated in the hydrophilic layer of the web to give a coverage of 3 mg. of silver nuclei per square foot is sufficient to cause complete removal of substantially all undeveloped silver halide from a silver chlorobromide negative material processed by such a web. As this coverage is increased up to 120 mg. of silver nuclei per square foot negative fog is lowered and the processing rate increases. Furthermore, the use of lead sulfide nuclei in a gelatin layer at a coverage of 8 mg. per square foot has been found to result in higher negative contrast when the same photographic material is processed. In turn, increasing the coverage of lead sulfide nuclei will increase the contrast and speed of the processed negative image, while lowering maximum density. The lead sulfide and Carey-Lea silver nuclei are the preferred silver precipitants when used at coverages of 3 to 120 mg. per square foot in the hydrophilic layer of the web.

The photographic webs of the invention may be prepared by coating a suitable support with an aqueous solution of the polymers. Silver-precipitating nuclei also can be dispersed in the solution. These polymers are useful as binders for light-sensitive salts such as silver halide and can be used in admixture with gelatin in any proportion. They can also be used with other compatible hydrophilic colloids. Other addenda may also be present in the coating solution, for instance, spreading agents (e.g., saponin, polyglycerol, monolaurate and the sodium salts of alkyl aryl sulfonates), buffers such as boric acid and the like.

The supports may take any suitable form or shape. For example, they may consist of sheets, strips or webs of glass, metal, paper, polyolefins such as polyethylene and polypropylene; polystyrenes; polyesters such as polyethylene terephthalate; cellulose esters and the like.

The support coated with the polymers may contain a subbing layer, if desired. Suitable subbing layers include, for example, those described in U.S. Pat. No. 3,143,421. Any suitable technique may be used for coating the polymer on the support as, for instance, by coating with applicator or transfer rolls, spray coating, brushing, etc.

Once the support has been coated with the coating composition of polymer and dried, it is then subjected to cross-linking in the presence of a hardener. The extent of cross-linking will vary with the particular polymer selected, but should be that degree of cross-linking that insolubilizes the polymer after coating. Hardeners for this purpose are cross-linking agents well known to those skilled in the art and include by way of example organic dialdehydes such as succinaldehyde, glutaraldehyde, o-phthalaldehyde and the like; ketone hardeners such as 2,5-hexanedione, p-benzoquinone and the like; sulfonate esters such as bis(methane sulfonates); sulfonyl halides such as bis(sulfonyl chlorides); active halogen compounds such as bis(chlorohydrins) and bis(2-chloroethylureas); active olefins such as divinyl sulfone, divinyl ketone, etc.; polymeric hardeners, dialdehyde derivatives of starch and other polysaccharides; inorganic hardeners such as chromium salts like chrome alum.

A preferred method of insolubilizing the polymer after coating is by use of dialdehydes which cross-link with the hydroxyl groups of the polymer to form acetal cross-links. In accordance with this method, the dried coating of the polymer is subjected to an aqueous, acidic hardening bath containing a

dialdehyde which as aforementioned cross-links the polymer in a swollen condition. Excess hardener and acid are removed by a wash and the web is then bathed in processing solution thus displacing the water and providing the finished processing element or web. If desired, preliminary to hardening by the coating in this manner, the coating may be pre-hardened by including in the coating composition any one of the aforementioned hardeners.

The processing solutions of the invention comprise alkaline solutions of one or more silver halide developing agents and a silver halide solvent. Certain other ingredients may also be present, for example, where foam on the processing solution is not a problem, it has been found that the addition of certain surface active agents to the processing solution improves the quality and effective sensitometric speed of the negatives obtained. Further, the addition of small amounts of potassium iodide to the processing solution modifies the deposition of silver in the web. In some instances, small amounts of potassium iodide have been found beneficial in eliminating a mirror-like coating which is formed on the surface of the negative. In addition, preservatives and buffers may be provided in the processing solution. Preferred materials providing efficient preservative and buffering action are the amine-sulfur dioxide addition products described in detail in U.S. Pat. No. 3,179,517, hereby incorporated by reference. These addition products are prepared by reacting a suitable amine and sulfur dioxide gas. Amines suitable for this preparation include primary, secondary and tertiary amines such as 2-aminoethanol, 2-methylaminoethanol, 2-dimethylaminoethanol, 2-ethylaminoethanol, 2-diethylaminoethanol, 2,2',2''-nitrilotriethanol, 2-aminoethylaminoethanol, 2,2'-iminodiethanol, 5-diethylamino-2-pentanol, 2-amino-2-methyl-1-propanol, morpholine and piperidine among others.

For the present invention, the preferred amine-sulfur-dioxide addition product is prepared in the following manner. Sulfur dioxide gas is slowly bubbled through one mole of the preferred amine, 2,2'-iminodiethanol, with adequate stirring until it adsorbs the equivalent of 0.25 mole of sulfur dioxide. The resulting 2,2'-iminodithioethanol-sulfur dioxide addition product contains the equivalent of 13 percent sulfur dioxide by weight, or 20 mole percent. When this amine-sulfur dioxide product is incorporated in typical processing solutions of the present invention, a pH from 9.0 to 9.5 is obtained.

The silver halide developing agents which may be employed in the processing solutions include methyl-p-aminophenol sulfate hydroquinone, chlorohydroquinone, diaminophenols, e.g., 2,4-di-aminophenol and 3,4-diaminophenol hydrochloride, glycerine, 1-phenyl-3-pyrazolidone and its derivatives, triaminophenols, including 2,4,6-triaminophenol, catechol, pyrogallol, gallic acid, paraphenylene diamines, enediols, such as ascorbic acid and combinations of these developing agents. Especially useful developing compositions comprise mixtures of mono-methyl-p-aminophenol sulfate and hydroquinone; 1-phenyl-3-pyrazolidone and hydroquinone; and especially 4,4-dimethyl-1-phenyl-3-pyrazolidone and hydroquinone.

Although any of the well-known silver halide solvents, e.g., alkali thiocyanate, alkali selenocyanates, thioglycerol, aminoethanethiols, etc., may be employed as a fixing agent in the processing solution of the present invention, the preferred solvent is hypo sodium thiosulfate pentahydrate. The concentration of this reagent in the processing solution may range from 2 to about 25 grams per liter with advantage. In most cases, for example, it has been found that about 8 grams per liter of sodium thiosulfate pentahydrate provides satisfactory clearing of the undeveloped silver halide with polymer webs of this invention whereas about 6 grams per liter is sufficient with gelatin webs.

When it is desired to store rolls of processing webs containing processing solution, care must be taken to prevent oxidation or drying of sections of the web which would cause incomplete development and fixation in use. Therefore, it is necessary that each convolution of web in a roll be in contact

over its entire surface with an adjacent convolution since any gaps provide access for air. The sides of the presoaked web roll must be protected against drying out and oxidation during storage, either by soaking the entire roll in an impermeable package or by the use of tight fitting pressure flanges. In addition to the obvious solution to the problem of eliminating gaps in the roll by careful winding of the web under suitable tension, it has been found that use of a duplitzed web is advantageous. A duplitzed web is one in which both surfaces of a film support, for example, are coated with a layer of the polymer. Such a web would be prepared for eventual use by soaking both absorbent layers in processing solution and then coiling the web upon itself under tension, thus assuring intimate contact between the hydrophilic layer on the outside of each coil and the absorbent layer on the inside of the succeeding coil of the web.

Although the novel processing element or web of the invention is particularly adapted for the preparation and storage of "wet" types, it should be apparent that the webs may also be prepared and stored in a dry condition. Webs of this type are prepared by soaking in a processing solution in the usual way and then drying the web to remove the free water. The web may be rolled or not, as desired, and stored in a convenient manner. Alternatively, the absorbent layer may be coiled with the processing solutions incorporated and then dried. Dry webs of this type containing all of the chemical ingredients of the processing solution may be readied for use by replacement of the necessary water in a variety of ways. For example, the moisture may be replaced by steaming the web prior to use or the web may be dipped in water briefly and the excess removed with a squeegee. A third method is to dip the negative to be processed in water, remove the excess with a squeegee or soft sponge and then apply the dry web to the moist negative. It has been discovered, surprisingly enough, that dry webs containing the chemical processing ingredients may be rendered suitable for use in the method of the invention by replacing less than one-half the amount of water originally present in the processing solution used in the preparation of the web. Webs containing the reduced amounts of water have been found to yield processed negatives sensitometrically equivalent to those processed with webs used directly after soaking, and the reduced amount of water present provides a processed negative which is substantially drier than those obtained in the usual way. On the other hand, a web soaked in a double-strength modification of a preferred processing solution, and permitted to absorb the same amount of the processing solution ingredients (except water) as when soaked in the normal solution, gives poor processing of the negative.

In addition to the presoaked webs and dry webs containing processing chemicals which are described above, the invention also includes webs composed of the absorbent layer containing only dispersed silver precipitating agent. Webs of this type are soaked in processing solution immediately prior to use.

Photographic development with the processing web or element of the invention is carried out by intimately contacting the web containing absorbed processing solution with a silver halide emulsion layer containing a latent image to develop the unexposed silver halide and to remove substantially all of the undeveloped silver halide. The processing element is maintained in intimate contact with the silver halide until development of the latent image is substantially complete and substantially all of the undeveloped silver halide has been cleared from the emulsion layer by the silver halide solvent and deposited in the processing element by the silver halide precipitating agent. The processing element is then separated from the substantially completely developed and fixed emulsion layer which requires no further processing of any kind.

The processing element or web of the invention is generally

applicable to the processing of photographic emulsions of the developing-out type. Various silver salts may be used as the sensitive salt, such as silver bromide, silver iodide, silver chloride or mixed silver halides such as silver chlorobromide or silver bromiodide. The emulsions are formulated according to known procedures and may include any of the usual addenda such as sensitizers, antifoggants, hardeners and the like. The photographic processing elements of the invention may also be employed to process silver salt-sensitized emulsion layers containing incorporated developing agent. In this embodiment, the silver halide developing agent is omitted from the processing solution since it is already present in the emulsion layer.

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

EXAMPLE 1

COPOLYMER PREPARED FROM POLY(VINYL ALCOHOL) AND SODIUM 2-SULFOBENZALDEHYDE

A solution of 100 g. of poly(vinyl alcohol) (Elvanol 71-30)* (*Elvanol 71-30 is 98.5 to 100 percent hydrolyzed PVA with medium range viscosity.) in 910 ml. of water containing 31.6 ml. of 85 percent phosphoric acid is prepared on the steam bath. To this is added with stirring 23.6 g. of sodium o-sulFOBENZALDEHYDE in a little hot water. The solution is kept at 60° C. for several days, then poured into isopropyl alcohol. The precipitated polymer, after vacuum drying, weighs 115.5 g. and contains 4.4 percent sulfur.

EXAMPLE 2

COPOLYMER PREPARED FROM POLY(VINYL ALCOHOL, SODIUM 2-SULFOBENZALDEHYDE AND CYANOACETAMIDOACETALDEHYDE DIETHYL ACETAL

A solution of 50 g. of poly(vinyl alcohol) (Elvanol 71-30) is prepared in 450 ml. of water, then treated with 12 g. of sodium o-sulFOBENZALDEHYDE, 16 ml. of 85 percent phosphoric acid, and then with 0.083 mole of crude cyanoacetamido acetaldehyde diethyl acetal. After keeping at room temperature overnight, the solution is poured into isopropyl alcohol, washed with fresh alcohol, then dissolved in 400 ml. of water for subsequent coating. A sample dried for analysis has S, 3.1 percent; N, 1.4 percent.

EXAMPLE 3

COPOLYMER PREPARED FROM POLY(VINYL ALCOHOL) AND SODIUM 4-METHOXY-3-SULFOBENZALDEHYDE

A suspension of 50 g. of poly(vinyl alcohol) (Elvanol 71-30) in 300 ml. of glacial acetic acid is treated with 20.6 g. of sodium 4-methoxy-3-sulFOBENZALDEHYDE and 10 ml. of 85 percent phosphoric acid. The mixture is stirred at 60° C. with the addition of 150 ml. of acetic acid to facilitate stirring of the swollen mass. After 2 hours, the solid is collected and washed with acetone to harden. The yield after vacuum drying is 75.5 g. The sulfur content is 3.7 percent.

EXAMPLE 4

COPOLYMER PREPARED FROM POLY(VINYL ALCOHOL) AND 2,4-DISULFOBENZALDEHYDE

A solution of 87 g. (1.01 moles) of poly(vinyl alcohol) in 203 g. of methanol is treated with the mixture obtained by adding 18.5 g. (0.6 mole) of sodium 2,4-disulFOBENZALDEHYDE to 25 ml. of concentrated hydrochloric acid and diluting with 25 ml. of methanol. The reaction is allowed to proceed at 60° C. overnight. The gel which is formed is chopped in a blender and the supernatant fluid kept neutral by the addition of 10 percent sodium hydroxide. After washing with several portions of methanol, the product is collected and sucked dry, then dissolved in 400 ml. of warm water. Found: S, 4.4 percent.

EXAMPLE 5

1-SULFO-4-AZONIA-6,6-DIETHOXYHEXANE

To a solution of 66.1 g. (0.5 mole) of aminoacetaldehyde diethylacetal in 250 ml. of acetonitrile stirred at room temperature is added 61.1 g. (0.5 mole) of 1,3-propane sultone over a period of 5 minutes. An exothermic reaction brings the solution to reflux (80° C.) for a few minutes after which it slowly returns to room temperature. Some product crystallizes while the mixture is stirred an additional 4 hours at room temperature. The mixture is filtered and the filtrate evaporated to an oil which crystallizes to a semisolid while standing overnight. An ether-acetone mixture is added to the mass to complete the crystallization. The two fractions are dried in vacuo and combined. The product weighs 110.2 g. (86.5 percent of the theoretical yield).

Calcd. for
C₈H₁₁NO₃S:
Found:

C, 42.4; H, 8.2; N, 5.5; S, 12.5
C, 42.1; H, 8.1; N, 5.5; S, 12.4

EXAMPLE 6

COPOLYMER PREPARED FROM POLY(VINYL ALCOHOL) AND 1-SULFO-4-AZONIA-6-OXOHXANE ACETAL (15 MOLE PERCENT ACETAL)

With stirring 44.1 g. (equivalent of 1 mole of hydroxyl groups) of poly(vinyl alcohol) (Elvanol 71-30) is dispersed in cold water. Warming on the steam bath provides a solution which is adjusted to 60° C. in a constant temperature bath. To the stirred solution is added 34 ml. of concentrated hydrochloric acid and 38.2 g. (0.15 mole) of the above acetal dissolved in 50 ml. of water. The stirred solution is kept at 60° C. for 2½ hours. The polymer is precipitated and washed thoroughly in isopropyl alcohol and dried in vacuo. The product weighs 59.6 g. (87 percent of the theoretical weight).

A 10 percent solution of the polymer in water is prepared by warming on the steam bath with stirring.

EXAMPLE 7

COPOLYMER PREPARED FROM POLY(VINYL ALCOHOL) AND 1-SULFO-4,4-DIMETHYL-4-AZONIA-6,6-DIETHOXYHEXANE

In a manner similar to Example 5 is prepared 1-sulfo-4,4-dimethyl-4-azonia-6,6-diethoxyhexane.

Calcd. for C₁₁H₂₃NO₃S:
Found:

N, 5.0; S, 11.3
N, 4.9; S, 11.2

A copolymer prepared from poly(vinyl alcohol) and this product (15 mole percent acetal) is obtained as in Example 6. It is found to contain 1.1 percent nitrogen.

In a similar method, poly(vinyl alcohol) is reacted with 1-sulfo-4,4-diethyl-4-azonia-6,6-diethoxyhexane.

EXAMPLE 8

COATING AND HARDENING OF THE COPOLYMER PREPARED IN EXAMPLE 6 - NO PREHARDENER

To 400 ml. of a 10 percent solution of the copolymer prepared in Example 6 is added 40 ml. of a 2 percent boric acid solution, 10 ml. of a physical development nuclei preparation, and a spreading agent. The mixture is coated on subbed support to a solids coverage of 1.9 g./ft.² and is ammonia-fumed before drying. The dried coating is hardened by a 3-minute room temperature immersion in an aqueous solution comprised of 0.096 M of succinaldehyde and 0.50 N hydrochloric acid.

The hardened web is washed 2 minutes in 70° F. water, and immersed 3 minutes in an imbibant comprising:

2,2'-Iminodiethanol-SO₂ addition product
(13 % SO₂ by weight)
2-Methylaminoethanol

150 cc.

40 cc.

Hydroquinone
Phenidone
Sodium thiosulfate pentahydrate
Diethylaminomethanethiol · hydrochloride
4,5-(2,3-D-fructopyrano)-2-oxazolidinethione
Water to

25 g.
2 g.
30 g.
10 g.
10 g.
1 liter

pH = 9.3

The amount of imbibant absorbed by the web (hereafter designated the pickup) is approximately 12 g./ft.². The highly swollen web is rolled in contact with an exposed strip of high-speed gelatine silver bromoiodo film. which is processed in 17 minutes.

EXAMPLE 9

COATING AND HARDENING OF THE COPOLYMER PREPARED IN EXAMPLE 7—NO PREHARDENER

To 400 ml. of a 10 percent solution of the copolymer prepared in Example 7 are added 40 ml. of a 2 percent boric acid solution, 5 ml. of a physical development nuclei preparation and a spreading agent. The mixture is coated on subbed support to a solids coverage of 1.4 g./ft.² and is ammonia-fumed before drying. The dried coating is hardened by a 10-minute room temperature immersion in an aqueous solution comprised of 0.192 M succinaldehyde and 0.142 N H₂SO₄. The hardened web is washed 5 minutes in 70° F. water and immersed 3 minutes in the imbibant described in Example 8. The pickup of imbibant is 15.1 g./ft.². The web is used to process an exposed strip of high-speed gelatine silver bromoiodo film.

EXAMPLE 10

COATING AND HARDENING OF THE COPOLYMER PREPARED IN EXAMPLE 7—PREHARDENED OVERCOAT

A length of the coating described in Example 9 is overcoated with a mixture consisting of 20 ml. of a 10 percent solution of the copolymer prepared in Example 7, 0.02 ml. succinaldehyde (the prehardener) and a spreading agent. The pH of the coating mixture is approximately 2. The mixture is coated on subbed support to a total solids coverage of 2.7 g./ft.² and allowed to dry at room temperature overnight. The coating is hardened in the same manner as in Example 9. The pickup of imbibant is 7.2 g./ft.² and the web is used to process an exposed strip of high-speed gelatine silver bromoiodo film.

EXAMPLE 11

COATING AND HARDENING OF THE COPOLYMER PREPARED IN EXAMPLE 4—PREHARDENED COATING

To 200 ml. of a 10.6 percent solution of the copolymer prepared in Example 4 are added 10 ml. of a physical development nuclei preparation, 1.0 ml. of 1 percent solution of succinaldehyde and a spreading agent. The pH of the coating mixture is adjusted to 1.75. The mixture is coated on a subbed support to a solids coverage of 1.3 g./ft.² and dried without ammonia-fuming. The dried coating is hardened by a 10-minute immersion at room temperature in a solution of 0.096 M succinaldehyde and 0.142 N sulfuric acid. The hardened web is washed 5 minutes in 70° F. water and immersed 5 minutes in an imbibant comprising:

2-Methylaminoethanol-SO₂ addition product
(20.3% SO₂ by weight)
Hydroquinone
Sodium Thiosulfate Pentahydrate
Potassium iodide
Methyl phenidone
3-Mercapto 1,2,4-triazole
2-Hydroxy-4-thiatetradecyltrimethylammonium
p-toluene sulfonate
Water to

160 ml.

15 g.
40 g.
0.4 g.
2 g.
0.05 g.

0.2 g.
1 liter

The pickup of imbibant is 7.4 g./ft.² and the web is physically tough compared to webs with no prehardener. This web is used to process an exposed strip of high-speed gelatine silver bromoiodo film.

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EXAMPLE 12

COATING AND HARDENING OF THE COPOLYMER
PREPARED IN EXAMPLE 4—PREHARDENED WITH
CHROME ALUM IN COATING

To 80 ml. of a 10.2 percent solution of the copolymer prepared in Example 4 is added a 5 percent solution (4ml. of chrome alum $[K_2Cr_2(SO_4)_4 \cdot 24H_2O]$ and a spreading agent. The mixture is coated on a subbed support to a solids coverage of approximately 2 g./ft.². The dried coating is hardened by a 5-minute room temperature immersion in a solution consisting of 0.384 M succinaldehyde and 0.284 N sulfuric acid. The hardened web is washed 5 minutes at 70° F. and immersed 5 minutes in the imbibant described in Example 11. The pickup of imbibant is 9.5 g./ft.² and the coating is physically tough.

EXAMPLE 13

COATING AND HARDENING OF THE COPOLYMER
PREPARED IN EXAMPLE 4—PREHARDENED COATING

To 800 ml. of a 10 percent solution of the copolymer prepared in Example 4 is added 200 ml. of water, 50 ml. of a dispersing physical development nuclei, 5 ml. of a 1 percent solution of succinaldehyde and a spreading agent. The pH is adjusted to 1.65 with dilute hydrochloric acid. The mixture is coated on subbed support to a solids coverage of 2.1 g./ft.².

A 50-ft. length of the dry 35-mm. coating is continuously passed through a hardening bath consisting of 0.115 M succinaldehyde and 0.284 N sulfuric acid, followed by a 70° F. water wash, and finally by a soak in the imbibant described in Example 11. The treatment of the coating in each bath is for 3 minutes. The resulting web has a pickup of 8.9 g./ft.² and is physically tough and resistant to abrasion. This web successfully processes a high-speed gelatine silver bromoiodo film.

The presoaked web is placed in a polyethylene-aluminum-paper laminated bag and incubated at 154° F. for 6 days. Examination of the web shows that the vehicle itself is apparently unchanged after this treatment. (A comparable gelatin vehicle web, incubated at 130° F. becomes mushy and unusable well within 24 hours.) The chemical stability of the poly(vinyl alcohol) webs toward imbibant is markedly greater than that of gelatin webs.

EXAMPLE 14

COATING AND HARDENING OF THE COPOLYMER
PREPARED IN EXAMPLE 1

To 20 ml. of a 10 percent aqueous solution of the copolymer prepared in Example 1 are added 0.25 ml. of a dispersing physical development nuclei, 2 ml. of aqueous 1 percent boric acid and 2 ml. of 0.016 M o-phthalaldehyde and a spreading agent. The mixture is coated on subbed support to a solids coverage of approximately 2 g./ft.². This coating, without further hardening, has an imbibant pickup of 3.3 g./ft.² and is stable to boiling water.

EXAMPLE 15

COATING AND HARDENING OF THE COPOLYMER
PREPARED IN EXAMPLE 2

In a manner similar to that of Example 14, the copolymer prepared in Example 2 is coated on subbed support to a solids coverage of 1.86 g./ft.². The coating is hardened by immersion

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in a 1 M sodium hydroxide solution. This treatment yields a coating with a pickup of 4.0 g./ft.² which resists treatment with boiling water and is stable after prolonged contact with an alkaline imbibant.

EXAMPLE 16

COATING AND HARDENING OF THE COPOLYMER
PREPARED IN EXAMPLE 3

In a manner similar to that of Example 14, the copolymer prepared in Example 3 is coated on subbed support to a solids coverage of approximately 2 g./ft.². The coating is hardened by immersion for 3 minutes at room temperature in a solution consisting of 0.50 N hydrochloric acid and 0.092 M succinaldehyde. The hardened web is washed 2 minutes in 70° F. water and immersed 2 minutes in the imbibant described in Example 11. The pickup of imbibant is 5.45 g./ft.² and the coating is stable both to boiling water and to imbibant.

EXAMPLE 17

SELF-SUPPORTED WEB OF THE COPOLYMER
PREPARED IN EXAMPLE 4

A copolymer prepared as in Example 4 is coated onto a glass plate at a coverage to produce a dried down coating which is 5 mils thick. The coating is stripped from the glass support and immersed in an acidic succinaldehyde solution (0.1 molar succinaldehyde and 0.1 molar sulfuric acid) for 10 minutes. It is then rinsed for 5 minutes in 70° F. water and without drying the unsupported web is immersed in the imbibant of Example 11. A portion of the web is used to process an exposed silver halide film by pressing it into intimate contact with the light-sensitive emulsion surface. Another portion of the web material is sealed in a vaportight package and stored for 6 days at 150° F. The unsupported imbibed web is unchanged after this incubation period and may conveniently be used for processing.

EXAMPLE 18

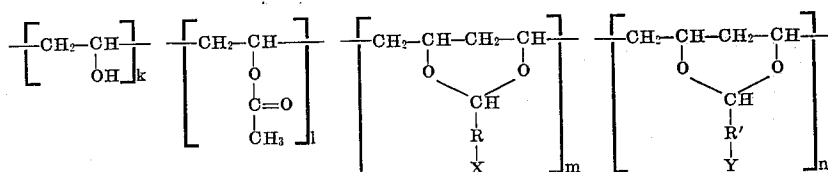
SELF-SUPPORTED WEB OF THE COPOLYMER
PREPARED IN EXAMPLE 4

A solution of 200 ml. of a 10.6 percent solution of the copolymer of Example 4 is acidified with sulfuric acid to a pH of 3.5. One ml. of a 1 percent succinaldehyde solution is added to the mixture which is cast on a polyester surface. After drying, the sheet is 4.0 mils thick. It is stripped from the polyester surface as a self-supporting web. Such a web is partially hardened to the degree that it may also be swollen by alkaline solution. Prior to use, it is treated in a hardening bath, as in the previous example, after which without drying it is imbibed with processing solution. In this manner, self-supporting webs may be cast and stored dry. Just prior to use they are further hardened and imbibed with processing solution to provide the necessary processing activity in the desired circumstance.

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

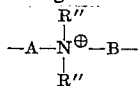
We claim:

1. A photographic processing web used in processing an exposed photosensitive element comprising a polymer composed of recurring segments:



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wherein k indicates about 64 to 95 mole percent, l indicates about 0 to 15 mole percent, m indicates about 5 to 20 mole percent, n indicates about 0 to 10 mole percent; X is SO_3^- or $-\text{SO}_3\text{Z}$ wherein Z is an alkali metal or hydrogen; R' is an alkylamino group; Y is a radical containing an active methylene group and R is a phenylene group or the positively charged portion of an inner salt having the structure:



wherein A and B are alkylene groups and R'' is hydrogen or an alkyl group, with the proviso that when R is the positively charged portion of an inner salt, X is SO_3^- .

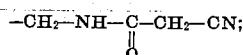
2. A photographic element of claim 1 wherein said layer is on a support.

3. A photographic processing web comprising the element of claim 2 wherein said absorbent layer contains a photographic processing solution.

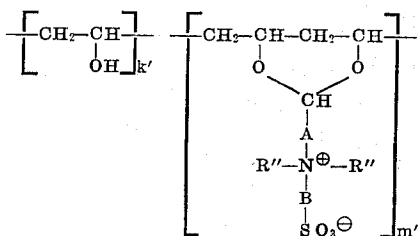
4. A photographic element of claim 1 wherein said layer comprises a silver precipitating agent.

5. A photographic element of claim 1 wherein said cross-linked polymer product is a dialdehyde cross-linked polymer product.

6. The photographic element of claim 1 wherein $-R' - Y$ is



7. A photographic element of claim 1 wherein the cross-linked polymer product is of a polymer composed of recurring segments having the structure:

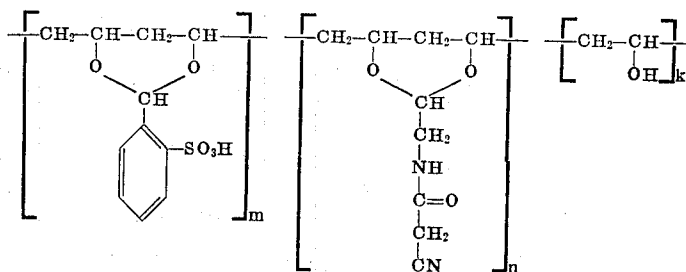


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wherein k' indicates about 80 to 95 mole percent, m' indicates about 5 to 20 mole percent, and A , B and R'' are as defined in claim 1.

8. A photographic element of claim 7 wherein said layer comprises an absorbent layer containing a photographic processing solution.

9. A photographic element of claim 1 wherein the cross-linked polymer product is of a polymer composed of recurring segments having the structure:



wherein k , m and n are as defined in claim 1.

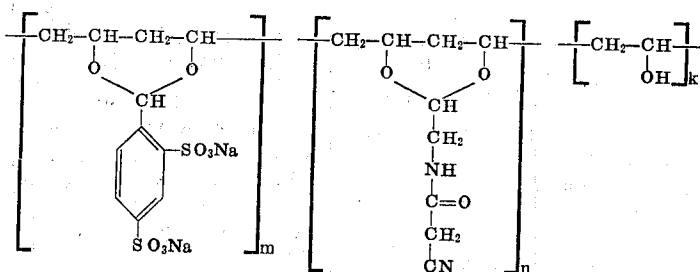
10. A photographic element of claim 9 wherein said layer comprises an absorbent layer containing a photographic processing solution.

11. A photographic element of claim 9 wherein the cross-linked product is a dialdehyde cross-linked polymer product.

12. A photographic element of claim 2 wherein said support is a polyester.

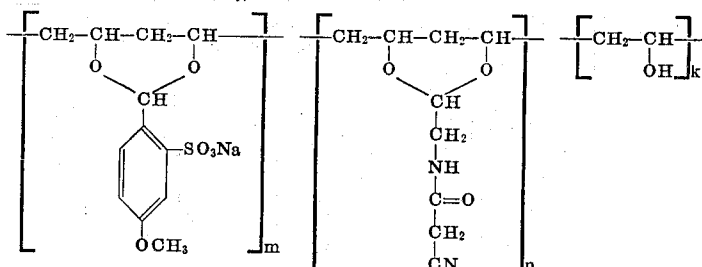
13. A photographic element of claim 2 wherein said element is provided with a sub layer for adhering said support to said layer.

14. A photographic element of claim 1 wherein said cross-linked polymer product is of a polymer having recurring segments having the following structure.



wherein k , m and n are as defined in claim 1.

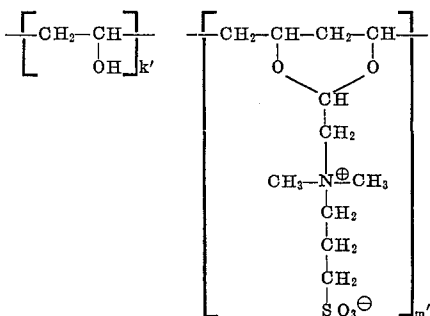
15. A photographic element of claim 1 wherein said cross-linked polymer product is of a polymer having recurring segments having the structure:



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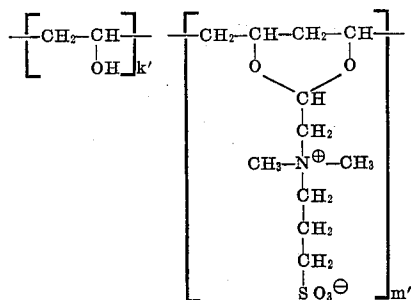
wherein k , m and n are as defined in claim 1.

16. A photographic element of claim 7 wherein said cross-linked polymer product is of a polymer having recurring segments having the structure:



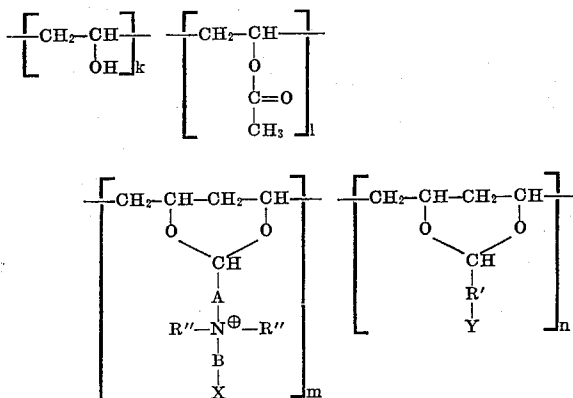
wherein k' and m' are as defined in claim 7.

17. The photographic element of claim 7 wherein the cross-linked polymer product is of a polymer having recurring segments having the structure:



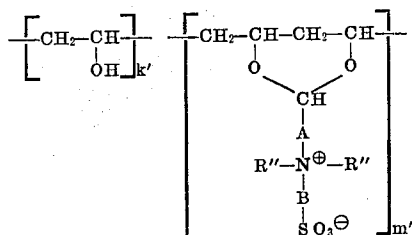
wherein k' and m' are as defined in claim 7.

18. A composition of matter comprising a polymer composed of recurring segments having the structure:



wherein k , l , m , n , A , B , R' , R'' , X and Y are as defined in claim 3.

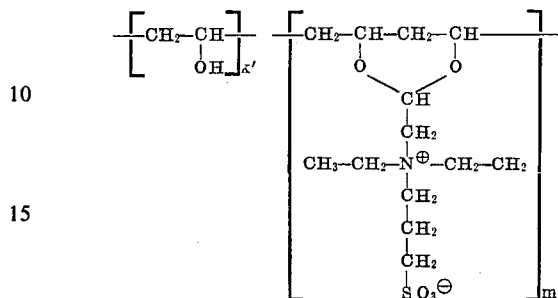
19. A composition of matter comprising a polymer composed of recurring segments having the structure:



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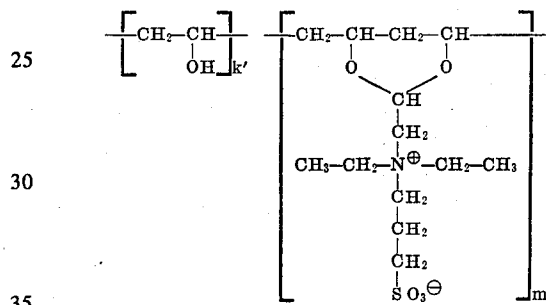
wherein k' indicates about 80 to 95 mole percent, m' indicates about 5 to 20 mole percent, and A , B and R'' are as defined in claim 3.

20. A composition of matter comprising a polymer composed of recurring segments having the structure:



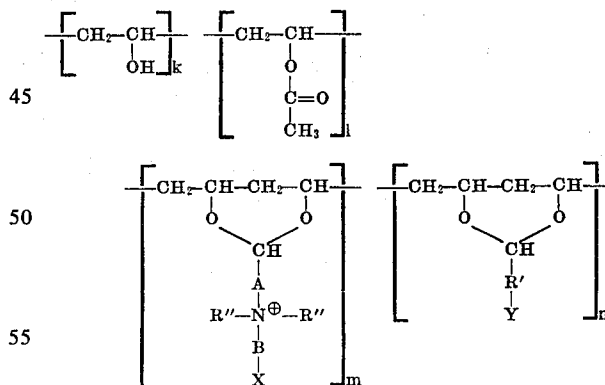
wherein k' and m' are as defined in claim 9.

21. A composition of matter comprising a polymer composed of recurring segments having the structure:

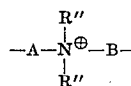


wherein k' and m' are as defined in claim 9.

22. A method of preparing a photographic processing web which comprises coating a support with a coating composition consisting essentially of an aqueous solution of a polymer composed of recurring segments having the structure:



wherein k indicates about 64 to 95 mole percent, l indicates about 0 to 15 mole percent, m indicates about 5 to 20 mole percent, n indicates about 0 to 10 mole percent; X is SO_3^- or $-\text{SO}_3\text{Z}$ wherein Z is an alkali metal or hydrogen; R' is an alkyl-amino group; Y is a radical containing an active methylene group and R is a phenylene group or the positively charged portion of an inner salt having the structure:



wherein A and B are alkylene groups and R'' is hydrogen or an alkyl group, with the proviso that when R is the positively charged portion of an inner salt, X is SO_3^- , and cross-linking said polymer in the presence of a cross-linking agent to effect hardening and water-insolubilization of said coating.

25. A method of claim 22 comprising incorporating in said composition a silver precipitating agent.

* * * * *

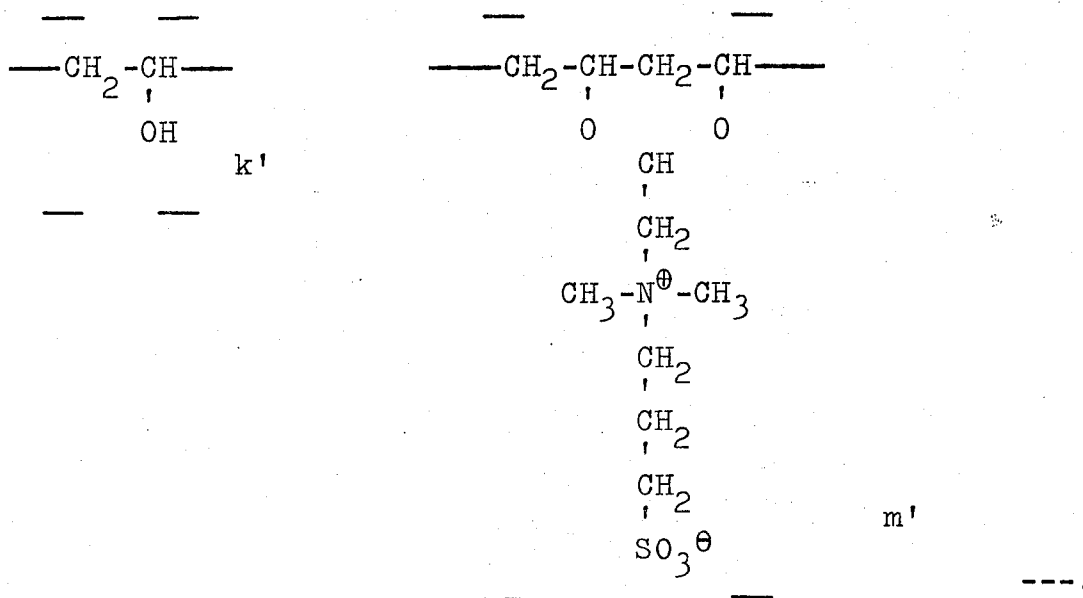
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,647,464 Dated March 7, 1972

Inventor(s) Donald A. Smith and Joseph A. Verdone

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

Top of Column 6, insert the following formula:



Column 15, line 28, delete "SO₃" and insert --SO₃^θ--.

Column 15, line 42, after the structural formula, delete " ; " and insert -- . --.

Column 15, line 3, delete "SO₃" and insert --SO₃^θ--.

Column 17, claim 16, second part of structural formula, delete "CH₃-N^θ-CH₃" and insert --CH₃-CH₂-N^θ-CH₂-CH₂--.

Column 17, line 41 through the bottom of Column 18 should be deleted.

Signed and sealed this 6th day of February 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents