Aug. 8, 1972 C. M. KOSTI 3,682,638

RADIOSENSITIVE FILM

Filed Dec. 3, 1970 2 Sheets-Sheet 1

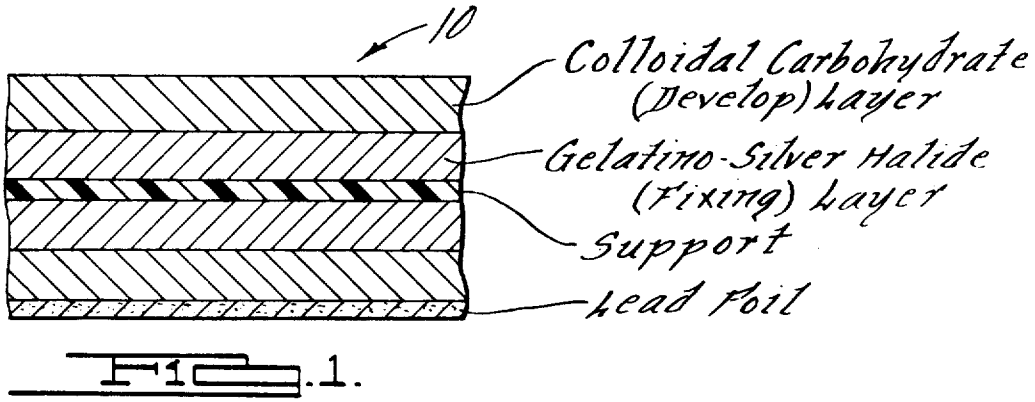


Fig. 1.

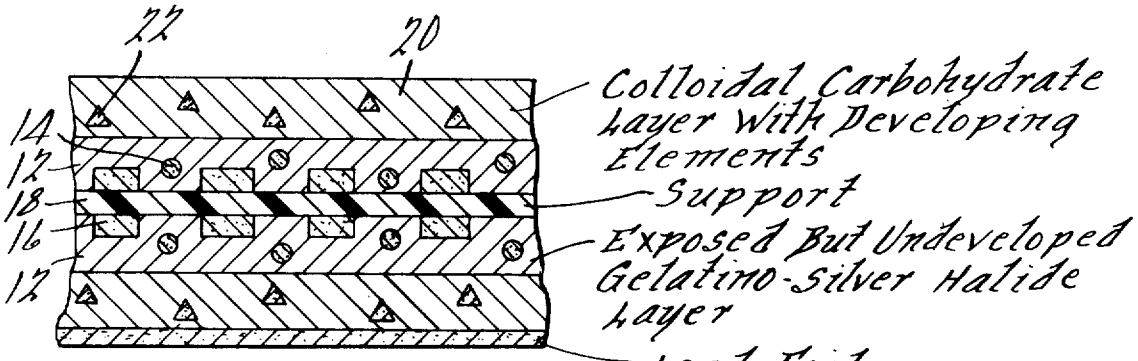


Fig. 2.

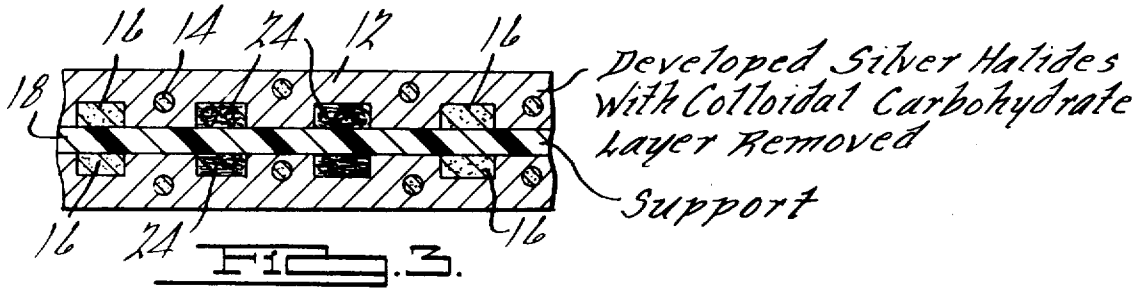


Fig. 3.

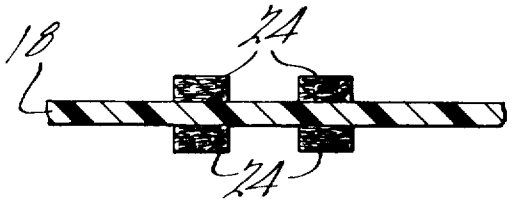


Fig. 4.

Final Permanent Negative With Exposed And Developed Silver Halides On Support

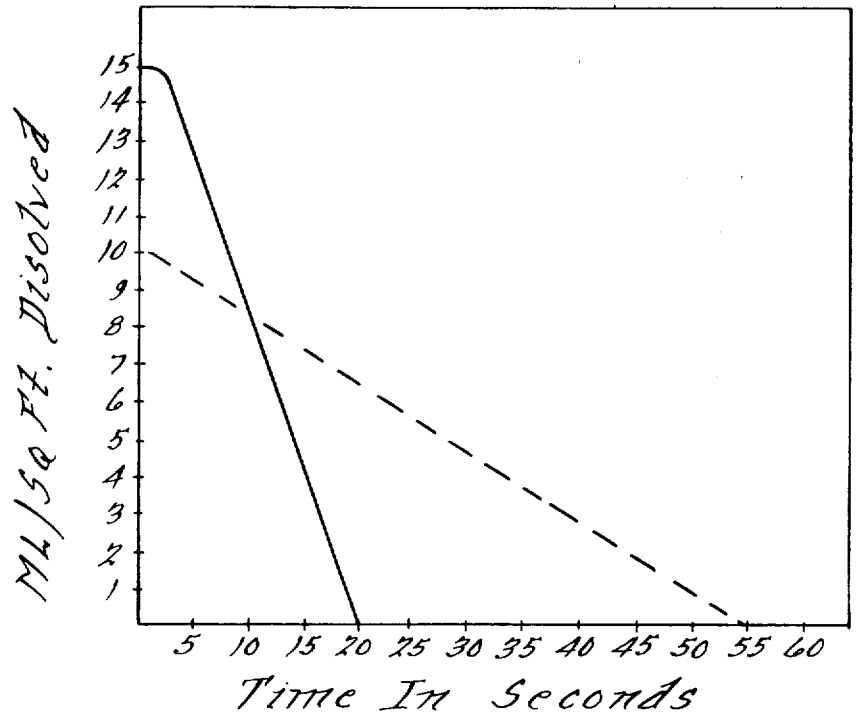
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RADIOSENSITIVE FILM

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Fig. 5.



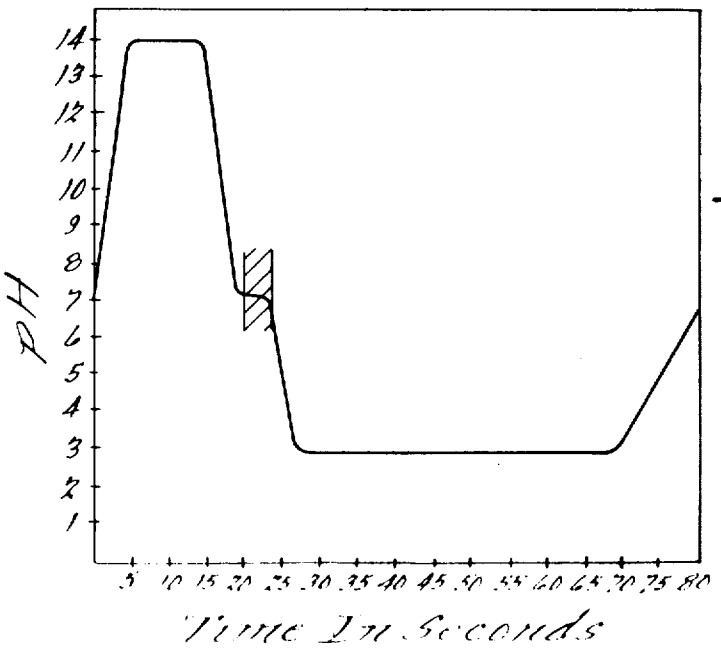


Fig. 6.

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United States Patent Office 3,682,638 Patented Aug. 8, 1972

3,682,638

RADIOSENSITIVE FILM

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Filed Dec. 3, 1970, Ser. No. 94,856
Int. Cl. G03c 1/06, 1/48, 5/38
U.S. Cl. 96—76 5 Claims

ABSTRACT OF THE DISCLOSURE

A film having both developing and fixing components contained within the water soluble gelatinous, collagenic or cellulose layers of the film. Upon exposure, the film is processed merely by contacting it with water for a few seconds. The film of this invention eliminates the requirement for developing by immersion in an aqueous alkaline solution and fixing by immersion in an aqueous acidic solution.

BACKGROUND OF THE INVENTION

A radiograph or radiosensitive film is a photographic film capable of registering an image when exposed to radiant energy of extremely short wavelength, for example, about 0.0001 the wavelength of light. Modern radiographic or X-ray films are made of an emulsion (gelatin containing a silver compound) and a transparent, blue tinted base. The base is a photosensitive film made from a cellulose derivative about 0.008 inch in thickness which provides the desired degree of stiffness and flatness for handling. The sensitive emulsion is made up of many grains or crystals of silver bromide or other silver halide material in gelatin, and the emulsion is generally coated on both sides of the base.

A dental radiosensitive film has a base coated generally on both sides with thin layers of gelatin having suspended therein the silver halide, and has a thin lead foil backing to minimize scattered or secondary radiation. The film is completely covered with a thin piece of black paper to prevent white light from exposing the film thus causing fogging. All these components, the film, lead foil and black paper are encased within a soft plastic packet. The total thickness of the entire packet is about 1.5 mm., and if soft rubber padding is used to line the inside the packet for more comfortable and less irritation to the tissue, then the thickness is about 2.0 to 2.5 mm.

During exposure, the radiant energy penetrates the front portion of the packet, the black paper, emulsion coating and film, the film, the back layer or emulsion, black paper and the free radiation energy is finally absorbed by the lead foil.

Upon exposure, therefore known radiosensitive film must be processed through the following steps to make the image visible and permanent: developing, rinsing, fixing, washing and drying. Accordingly, the film must be placed in a developer solution to convert the invisible image to a visible one composed of minute masses of black metallic silver. After contact with the developer, the film must be rinsed to remove excess developing solution and prevent fixer contamination. Next the film must be placed in a fixing solution to remove the unexposed silver halide therefrom and then be washed again to remove the processing chemicals and prevent eventual discoloration and fading. The film is then dried.

The difficulty with present radiosensitive films can be appreciated from the foregoing discussion. Thus, after exposure, it is necessary that the film be processed with several chemical solutions. Too little or too much contact with either the developer or fixer, or improper coating results in a poor image. More importantly, the practicing physician or dentist, while needing the developed film as

quickly as possible, is forced to send the film out for processing or maintain a developing studio in which he can carry out film developing—a task for which he is ill-prepared both in terms of time and training.

SUMMARY OF THE INVENTION

This invention relates to a process, and a radiographic film, for registering images on radiosensitive elements on a radiographic support, and more specifically to a process and film capable of producing a permanent negative on said support by a novel developing and fixing method.

Another object of this invention is to provide a simplified and foolproof method of eliminating over or under developing and fixing of radiographic exposures.

It is also another object of this invention to provide a permanent registration of an image on a radiographic support by a novel process utilizing a gelatinous colloidal hydrophilic protein layer and a colloidal hydrophilic carbohydrate layer.

It is a further object of this invention to provide an image on a radiosensitive support employing superimposed alkaline and acid layers.

Yet another object is to activate the developing process without submerging the exposed radiosensitive film in an alkaline solution, and to activate the fixing process without submerging the exposed radiosensitive film in an acid solution as is heretofore the usual accepted method.

It is still another object of this invention to incorporate the developing elements in a hydrophilic colloidal carbohydrate layer and to incorporate the fixing elements in a hydrophilic colloidal protein gelatino-silver halide layer.

More particularly, the object of this invention is to produce images on medical and dental radiographic films by improved developing and fixing processing.

The process and composition of the invention is a radiographic film having a support, a colloidal gelatino-silver halide emulsion layer on one or both sides of the support, and a hydrophilic colloidal carbohydrate layer positioned further from the support and on top of the emulsion layer. In dental or medical films, a lead foil is generally positioned on one side of the film above the carbohydrate layer. The colloidal hydrophilic carbohydrate layer is made alkaline in reaction and contains the developing crystals suspended therein, and the gelatinous hydrophilic protein layer is made acid in reaction and contains the fixing crystals suspended therein.

In the process of this invention, the radiosensitive elements in the hydrocolloidal gelatino-silver halide acid layer are exposed to a source of radiation to form a latent image on the support. The film is then placed under running water having a temperature in the range of about 80° F.–140° F., which, by virtue of hydrocolloid dissolution, activates the developing crystals within the hydrophilic colloidal carbohydrate layer. The latent image on the gelatino-silver halide emulsion layer is then converted to black metallic silver by the chemical action of the developing crystals on the exposed silver halides. At this state, the gelatinous emulsion is inactive to the alkaline solution (only the silver halide exposed to the radiation are acted upon) and becomes active only when the hydrophilic colloidal carbohydrate layer is completely washed away and the pH of the environment is almost neutral. The gelatino-silver halide layer, being acid-water soluble, now is brought into solution and reacts with the unexposed silver halides in the emulsion and by chemical dissolution removes them from the support.

DESCRIPTION OF THE DRAWINGS

Other features and advantages of the present invention will be made more apparent as this description proceeds,

reference being had to the accompanying drawings wherein:

FIG. 1 illustrates a cross section of a dental radiographic film constructed in accordance with teachings of this invention;

FIG. 2 is an enlarged view similar to FIG. 1 showing the developing crystals in an alkaline hydrophilic colloidal carbohydrate layer and the fixing elements in the gelatino-silver halide acid layer which is coated on the support of the radiosensitive film;

FIG. 3 illustrates the developing hydrophilic colloidal carbohydrate alkaline layer completely washed away and the developed-exposed silver halide and undeveloped-unexposed silver halide crystals in the gelatino-silver halide emulsion on the radiosensitive support;

FIG. 4 illustrates the permanent negative image on the radiosensitive support after the unexposed silver halide crystals have been removed by the fixing elements and the unhardened and unexposed silver halide emulsion washed away;

FIG. 5 illustrates the relative solubility of the developing and fixing layers of the radiosensitive film of this invention; and

FIG. 6 illustrates pH variations during the developing and fixing stages of the process of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In utilizing the process and film of this invention, and in reference to FIGS. 1 through 4, the film indicated generally by reference numeral **10** is exposed to radiation to produce a latent image on the radiosensitive emulsion **12** comprising fixing crystals **14** and silver halide crystals **16** on the support **18**. After exposure, the film is placed under running water having a temperature in the range of 80° F. to about 140° F., and more preferably 108° F. to 126° F., thereby placing the alkalimity of the hydrophilic colloidal carbohydrate layer **20** in solution and activating the developing crystals **22** to chemically convert the exposed silver halide **16** to black metallic silver **24** and creating a negative image or support **18**. During the developing process the gelatinous emulsion layer **12** is not affected by the alkaline superimposed hydrophilic colloidal carbohydrate layer **20** until said layer **20** is completely washed away thereby allowing the water to dissolve the fixing crystals **14** which then act directly upon the unexposed silver halide **16**. The unaffected and unhardened portion of layer **12** are both removed by the warm water, leaving only the hardened and developed metallic silver **24** on the support **18**. The entire process of developing and fixing lasts for only 1 to 1.5 minutes, depending on the temperature of the water, and results in a clean, well defined permanently fixed radiograph.

The developer used in this invention may be any of the commercially available water soluble developers now known to the art. Examples of a suitable developer include 4-phenyl catechol, N-beta hydroxy gentisamide, gentisamide, gentisaldoxime, 4-tertiary butyl catechol, 3-methoxy catechol, 4-hexylpyrogallol, 2-phenoxy hydroquinone, 4,4' - (2,3 - dimethyl tetramethylene) dipyrocatechol, nordihydroquaiaretic acid, toly-duro-xylo, cumohydroquinones, 3,4-dihydroxy diphenyl, 2,5-dihydroxy diphenyl, 2,3-dihydroxy diphenyl and 6,7,8 - tetrahydro naphthohydroquinone. The preferred developer for use in the film of this invention is p-methylaminophenol sulfate.

Alkaline materials are used to adjust the alkalinity of the hydrophilic colloidal carbohydrate layer to a pH in the range of about 9 to 14. Examples of such materials are the metallic carbonates and hydroxides such as sodium carbonate, sodium hydroxide, potassium carbonate, potassium hydroxide and combinations thereof.

The preferred material for use as the hydrophilic colloidal carbohydrate layer which contains the developing elements is sodium polymannuronate (sodium algenate). Sodium polymonnuronate is a derivative of polymonnuronic acid which can be regarded as a polymer containing varying proportions of D-mannuronic acid and L-guluronic acid. Polymonnuronic acid is very slightly soluble in water but freely soluble in alkaline solutions. It is capable of absorbing 200–300 times its weight of water, and the sodium, potassium, ammonium and magnesium salts are very soluble in water, forming a viscous, colloidal solution insoluble in aqueous acid solution but soluble in alkaline solution.

Other substances which can be used in place of sodium polymannuronate are hydrophilic carboxylated cellulose derivatives such as cellulose ether phthalate, methyl cellulose, ethyl cellulose, polyvinyl alcohols and like water and alkali soluble dibasic acid esters of ethyl cellulose including ammonium, alkali metals and amine salts of such dibasic acids as phthalic, maleic, and succinic acids.

The gelatino-silver halide emulsion employed in the light sensitive layer containing the fixing elements processed in accordance with this invention preferably has a pH in the range of about 9 through 14, and can be gelatino-silver chloride, gelatino-silver chlorobromide, gelatino-silver chloroiodide, gelatino-silver chlorobromoiodide, gelatino-silver bromide, and gelatino-silver bromoiodide emulsions of the developing out type. Such emulsions can be prepared by well known methods as taught in such patents as U.S. Pat. No. 2,618,556. The speed and the average gradient of the film emulsion is determined by the applicable methods contained in American National Standard Method for the Sensometry of Medical X-Ray Films pH 2.9—1964. The speed of the emulsion shall be as indicated in 1.2.1 and the average gradient shall be not less than about 1.5.

The support, or base, of the subject light sensitive elements processed in accordance with this invention can be any of the common supports used for photographic and radiographic products including cellulose nitrate film, cellulose acetate film, polyvinyl acetate film, polystyrene film, polyethylene terephthalate film and related films of resinous materials as well as glass, paper, metals, and others. The support should be of some safety type as defined by American National Standard Specifications for Safety Photographic Flm pH 1.25—1965. The thickness of the support is generally not less than about 0.10 mm. (0.004 inch) nor more than about 0.23 mm. (0.024 inch).

The lead foil, or other equally flexible material with equivalent X-ray attenuation characteristics as measured at 90 kilovolt peak, is not less than 0.060 mm. (0.024 inch) thick.

The following example will serve to explain and better illustrate the invention.

EXAMPLE

A radiographic element according to this invention was prepared as follows:

A support of cellulose material, namely cellulose acetate film, 0.008 inch thick was coated on both sides with a gelatino-silver chloride emulsion containing one mole of silver per 3.5 kilograms of emulsion. The emulsion may be modified by the incorporation of optic sensitizers such as green sensitizer, cyanine or mercuro-cyanine sensitizers, or chemical sensitizers such as sulfur, gold, etc. or other common emulsion addenda. The formula and the concentrations of the ingredients by weight of the gelatino-silver chloride layer was as follows:

Gelatino-silver chloride emulsion	g./mole	3500
Silver emulsion	g.	182
Fixer dispersion	cc.	70
Saponin solution (15%)	cc.	20
Water	cc.	103

The fixer dispersion was prepared with 25 g. of commercially available fixer containing ammonium thiosulfate, acetic acid, potassium allum, and sodium sulfite dissolved in 150 cc. of methyl alcohol, which was then dispersed in 500 cc. of 10% photographic gelatin and 50 cc. of 7.5%

saponin solution. The acidity of the fixer dispersion should be in the range of pH 2–4 and in this case the pH was adjusted to about 3. The two emulsions, the gelatino-silver chloride emulsion and the fixer emulsion, were remelted at about 42° C. which is the temperature above the gelation phase of gelatin, and were mixed completely so that the fixing elements and the silver chloride crystals were distributed evenly and homogeneously. There is no interaction between the two emulsions since gelatin is insoluble in organic solvents thereby permitting homogeneous incorporation of the two emulsions without the acidity of the fixer emulsion chemically reacting on the silver chloride crystals of the gelatino-silver chloride emulsion. In the event that the gelatin has poor physical properties, 10% formaldehyde may be added slowly until the proper hardness is attained. The emulsion was coated on both sides of the support at a concentration of 10 cc. per square foot.

Superimposed on both sides of the light sensitive emulsion layer was a hydrophilic colloidal sodium polymannuronate layer containing developing elements, saponin solution, water, and other hardening and plasticizing addenda. The sodium polymonnuronate was the sodium salt of polynannuronic acid (alginic acid). The composition of the sodium polymannuronate layer was prepared as follows:

	G.
Sodium polymonnuronate (sodium alginate)	12
Diatomatous earth	70
Borax	0.2
Sodium carbonate, to adjust to pH 14.	

60 g. of this powder was mixed with 200 cc. of room temperature 20° C. water for about 4 to 7 minutes until gelation occurred. The developer, para-methylaminophenyl sulfate was employed in this instance, 15 g. of which was dissolved in 118 cc. of water at about 52° C. with continuous stirring until the chemicals are dissolved completely and solution is uniform. 82 cc. of water was then added to bring the total volume of the solution to 200 cc., and the solution allowed to cool to room temperature befor the 60 g. of the polymonnuronate powder was added to the solution. Sodium carbonate used to adjust the alkalinity of the gel will retard the gelation time appreciably allowing for more working time with the suspension. The emulsion was then coated on both sides of the gelatino-silver chloride layer at a concentration of 15 cc. per square foot.

The purpose of the diatomaceous earth is to act as a filler to increase the strength and the stiffness of the polymonnuronate gel, to produce a smooth texture, to insure a firm surface that is not tacky, and to prevent syneretical exudate on the surface of the gel.

Borax, or almost any organic or inorganic borate, is added to further increase the strength and the density of the gel.

Plasticizers such as stearic acid, glycerol, glycerin, glycols, and other related compounds may be added to impart sufficient plasticity to the polymonnuronate gel and to retain the moisture in the gel.

Hardeners such as 10% formaldehyde may be further added to ensure the desired physical property of the gel.

A thin lead foil 0.024 inch thick was applied on one side of the polymonnuronate gel before the gel hardens. The lead foil is placed naturally so as to be on the side further away from the X-ray tube than the film. This foil applies only in producing of dental radiographic films; films used for medical radiographic purposes do not require a lead foil.

The radiographic element prepared as described above was exposed to an ionizing radiation at 60 kilovolts and 15 milliamperes for 0.2 second. The resultant exposed element was placed under running tap water having a temperature in the range of 108–126° F. thereby activating the developing elements embodied into the polymonnuronate layer. The hydroxyl group (alkaline ions) in the polymonnuronate layer activates the developing elements which instantly react chemically with the radiation exposed silver chloride crystals converting them to black metallic silver which results in negative image. The gelatin in the gelatino-silver chloride layer, being alkaline insoluble, will not be affected by the developing process until the entire polymonnuronate layer with the developing elements is completely washed away. The developing time at 108–126° F. water is about 20 seconds; this is the time necessary to dissolve the polymonnuronate layer completely. This is shown graphically in FIG. 5 where the solid line indicates the dissolution of the polymonnuronate sodium layer with the developing elements suspended within. It is the duration of the developing stage in the invention. The broken line illustrates the dissolution of the unexposed and undeveloped gelatino-silver chloride layer with the fixing elements suspended within, and is the duration of the fixing stage of this invention. Sodium polymonnuronate having the characteristic of absorbing water 200 to 300 times its weight, will swell as it absorbs water keeping the developer longer in contact with the radiation exposed silver chloride crystals resulting in far better detail contrast and density and less possibility of fog formation on the negative image. Once the complete wash of the polymonnuronate layer was affected, the warm water begins to dissolve the gelatin in the gelatino-silver chloride layer placing the ammonium thiosulfate, acetic acid, potassium allum, and sodium sulfite fixing elements in active state. Ammonium thiosulfate will dissolve the radiation unexposed and undeveloped silver chlorides more rapidly than the exposed silver chloride, acetic acid will speed up the dissolution of gelatin and serve as a neutralizer or barrier to the alkaline reaction during the developing stage, and the potassium allum will harden and shrink the gelatin around the radiation exposed and developed silver chloride crystals resulting in a permanent negative image.

The above processing can be appreciated more easily by reference to FIG. 6 wherein the shaded area illustrates the relative acid-base inactivity in this invention. It is the period of post development stage and pre-fixing stage where the pH of the packet is neutral. It is the period lapse of complete exhaustion of the developing elements in the polymonnuronate sodium layer and beginning of dissolution of the gelatino-silver chloride layer and activation of the fixing elements.

The pH of the radiographic film before the developing stage is neutral ((pH 7). When the film after exposure is placed under running tap water having a temperature of between 108–126° F. only 5 seconds will expire for the waterproofing outer protective layer to be dissolved and instantly the pH of the developing polymonnuronate sodium layer will sharply increase from pH 7 to nearly pH 14 where it remains during most of the developing stage. As some of the most outer developing elements are dissolved by the running warm water, equal amounts of the developing elements will be brought into the solution keeping the pH close to 14; however, when more of the developing elements are dissolved by the water and removed from the polymonnuronate sodium layer then are brought into the solution to maintain the pH equilibrium, and as more of the developing layer is removed the pH of the system will sharply drop until it reaches the pH of 7 when the polymonnuronate sodium layer is completely exhausted. This point indicates the end of the developing stage. There is approximately one to five seconds of relatively chemical inactivity following the developing stage until the water begins to dissolve the gelatin in the gelatino-silver chloride layer activating the fixing elements suspended within the gelatin layer. Here again the pH of the radiographic film will sharply drop from nearly neutral (pH 7) to the pH 3 indicating the commencement of the fixing stage. At this pH 3 the film will remain until most of the gelatin layer is

removed from the support when it will once again increase sharply to pH 7 indicating the end of the fixing stage and permanent negative fixation of the radiographic film.

The tanning properties of the developing agents presently commercially available are not strong enough by themselves to tan the exposed silver chloride and the gelatin surrounding it in the short time allowed in the context of the present invention; therefore, potassium allum is employed in the invention to produce a more effective and improved tanning and hardening property of the radiographic element resulting in denser, clearer, and better defined permanent negative which is vital for medical and dental diagnostic purposes. The washing away of the gelatino-silver chloride layer unaffected by the developing state took only 60 seconds which made possible viewing of the radiographic film less than 1.5 minutes from the time of exposure. The resultant radiographic film made in accordance with this invention produced a sharp, clear, and well defined negative image.

The entire radiographic element prepared as described above was only about 1.5 mm. (0.06 inch) thick and can be treated with waterproofing materials such as polyethylene glycol and other glycol derivatives, synthetic resins for example of the coumerone-indene resin type, paper, plastics, and other. Coumeron-indene resin has been used with excellent results to coat the surface of the radiographic film. It has excellent waterproofing properties and is readily plasticized with stearic acid and softens at 108–126° F. range of temperature. Coumerone-indene resin will prevent syneresis (loosing water by evaporation) and imbibition (sorption of water from air) reducing the possibility of dimensional changes of the hydrophyilic colloidal gelling materials used in accordance with this invention resulting in longer lasting radiographic element. Coumeron-indene resin is not toxic to mucous membrances when used in dental radiographs and does not react chemically with the underlying hydrophilic colloidal sodium polymonnuronate layer.

Materials which can be used in lieu of gelatin as a vehicle for the silver halide crystals must be capable of being hardened by oxidizing tanning developers, be acid and water soluble but alkaline insoluble, and be insoluble in organic solvents. Typical materials meeting these criteria are colloidal albumen, starch and starch derivatives.

It will be apparent from the foregoing that neither double exposure no emersion in alkaline solution of the light sensitive elements is necessary (in fact, such conditions must be avoided) to produce a well defined permanent negative image by this invention. Moreover, it is believed that the incorporation of a fixing element in the gelatino-silver halide emulsion on a radiographic support is unique, as is the employment of integral alkaline and acid layers containing the developing and fixing materials.

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

I claim:

1. A radiographic element for producing a radiographic image comprising a support, a gelatino-silver halide emulsion layer on at least one side of said support, and a hydrophilic carbohydrate layer positioned on the same side of same support and further from said support than said emulsion layer, said gelatino-silver halide emulsion having a pH less than 7 and containing dispersed therein a fixer, and said carbohydrate layer having a pH greater than 7 and containing dispersed therein a developer.

2. A radiographic element according to claim 1 wherein the hydrophilic carbohydrate is sodium polymonnuronate.

3. A radiographic element according to claim 1 wherein the gelatino-silver halide emulsion containing the fixer has a pH in the range between about 1 through 6, and wherein the hydrophilic carbohydrate layer containing the developer has a pH in the range between about 9 through 14.

4. A radiographic element according to claim 1 in which said layer of gelatino-silver halide emulsion and said layer of hydrophilic carbohydrate is positioned on each side of said support and wherein a lead shield is positioned on one side of said support against the othermost side of said carbohydrate layer.

5. A radiographic element according to claim 1 wherein said support is a material selected from the group consisting of cellulose nitrate, cellulose acetate, polyvinyl acetate, polystyrene and polyethylene terephthalate; wherein said hydrophilic carbohydrate is sodium polymonnuronate and said developer is selected from the group consisting of methylaminophenol sulfate, hydroquinone, pyrocathechol, catechol, gentisamide, hydroxylamine and pyrogallol, and wherein said fixer is a reducing agent.

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U.S. Cl. X.R.

96—61, 66, 95; 250—69