PAPER RADIOGRAPHIC ELEMENT CONTAINING SILVER HALIDE GRANES RHODIUM SALT SENSITIZED, THIOETHER RIPENED AND POLYVALENT METAL ION STABILIZED

ABSTRACT OF THE DISCLOSURE

Disclosed are improved radiation-sensitive image recording elements particularly useful in non-destructive testing which elements comprise a support carrying a thioether ripened, polyvalent metal ion stabilized radiation-sensitive silver halide layer of low coating density dispersed in a hydrophilic colloidal layer of substantially higher coating density. The silver halide grains are coarse grained and the elements can optionally contain incorporated developer agents and can optionally be combined with integral or non-integral luminous phosphor-containing intensifying screens. Processes for non-destructive testing and image recording are likewise disclosed.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to radiographic image-recording elements and to processes employing such materials. In one aspect, this invention relates to radiographic elements comprising single-sided silver halide coatings and optionally containing luminous intensifying screens. In another aspect, this invention relates to radiographic recording systems primarily designed for non-destructive testing and industrial use, which systems contain low silver content which unexpectedly provides improved characteristics to said systems.

Description of the prior art

In recent years the growth of mass production methods and trends toward automation of industrial processes have made necessary the rapid and large scale examination and testing of components and assemblies produced by such methods. By such testing, a manufactured item of equipment can be examined in order to determine the nature of its future use and to provide an estimate of its expected working life. One particular method of testing involves the examination of articles by procedures which do not impair the usefulness for future applications of the article itself. This nondestructive testing includes the use of radiological methods, mechanical methods, electrical and magnetic methods, visual methods, and the like. Regardless of the type of testing employed, they are all interested in defect detection and location. The composition, size and location of components and the particular physical state of the article under test likewise play an important role in the selection of testing methods employed. While the versatility of radiography as an inspectional method is a most outstanding feature, there have been substantial limitations on its use, which limitations have been primarily determined by the types of material examined and the type of flaw sought to be detected.

As a practical matter, however, radiographic material has been selected primarily on the basis of balancing the opposing factors of high quality in the image recorded and short exposure time to the object being tested. For example, a high quality film requires a slower, finer grained element and where a short exposure time is sought, a faster element would be required. In the past, this demand for high radiographic quality or short exposure time has found general acceptance by employing radiographic films usually coated on a cellulose acerate support and coated on each side with a radiation sensitive material, such as silver halide. With the increased cost of silver and the great need for more routine testing of mass produced items, cost becomes an important factor along with the faithful reproduction of the object tested. Furthermore, an image of lasting quality is an essential requirement so that good contrast and high photographic properties are imparted to important aspects in industrial radiographic elements. Hence, the emphasis on critical examination of large and sometimes inaccessible metal objects has been largely accomplished by employing radiographic films having the qualities of good definition, high contrast, maximum density and moderate developing time. It is not surprising therefore that fine grain, high contrast films such as Kodak Industrial X-ray film Type M have been developed for use in direct exposure or with lead foil screens having a silver coverage on each side of their supports of about 900 milligrams/square foot. This has led to a general acceptance that the best type of industrial radiographic element is one which is thickly coated with a fine grain silver halide in order to give high contrast and reduce the general exposure time.

Nevertheless, there has been a continuing and unsatisfied need for a radiographic element particularly suitable for nondestructive testing, which element is relatively inexpensive, highly sensitive to direct and screen type exposure and is capable of providing readily accessible images of high quality on site, that is, away from the laboratory darkroom.

It could not have been expected that an improved radiographic system could be achieved by employing a thinner, that is, less densely coated silver halide element having extremely good contrast and high speed. This unexpected aspect is particularly so in the utilization of single sided elements rather than the widely used double coated elements.

It has been known to use improved precipitation methods and stabilization methods along with techniques in ripening stages in order to produce high speed, high contrast emulsions. For example, in U.S. Patent 3,512,289, issued Sept. 29, 1970 to Wood various thioether and rhodium salts are utilized during the emulsification step and the digestion step to provide an improved process for making developing-out type photographic emulsions. Likewise, in U.S. Patent 3,748,709, issued to Sidebotham and in U.S. Pat. 3,574,625, issued Apr. 13, 1971 to Bacon, various polyvalent metal ions such as divalent, trivalent and tetravalent metal ions are utilized to stabilize the silver halide emulsions after the halide has been precipitated.

Those skilled in the art will readily appreciate that not all high contrast and fast emulsions can be utilized for radiographic applications. For example, high speed projection emulsions such as those particularly useful in photographic printing papers like enlarging papers, or designed for typesetting use, such as those disclosed in Sidebotham (U.S. 3,488,709) are unsuitable for radiographic use because emulsion streaking and structure and quantum mottle, unobjectional for enlargements and non-contact application, are wholly intolerable for reproducing radiographic images in nondestructive testing.

SUMMARY OF THE INVENTION

In accordance with the present invention there is provided an improved photographic image-recording element which comprises a support bearing one sided thereof a radiation sensitive silver halide layer of low coating density dispersed in a hydrophilic colloidal of a proportionately higher coating density. The element described herein...
is possessed of high speed, high contrast, and extraordinary physical characteristics which render it uniquely adaptable to industrial radiography and in particular the nondestructive testing of metal objects. The element so described comprises an incorporated developer and light sensitive layer which can comprise an integral or non-integral luminescent intensifying screen to enhance the image forming process. This element provides unexpected improvements in the marked decrease in quantum mottle without impairing the intricately balanced system of speed, image sharpness and contrast at the expense of prolonged exposure to radiation such as X-rays and gamma rays.

It is one object of the present invention to reduce the quantum mottle of radiographic products and systems with the other objects of this invention to provide improved photographic elements and, in particular, radiographic elements and processes employing said elements by providing unexpectedly superior image recording characteristics therein.

It is yet another object of this invention to provide a unique product for the nondestructive testing of materials which product comprises a combination of thickened hydrophilic colloid layer having dispersed therein a decreased coverage of light sensitive silver halide.

It is yet another object of this invention to provide a vastly improved nondestructive testing device for industrial radiography which comprises a paper radiographic element capable of producing a high quality image quickly, conveniently, inexpensively and accurately.

Still other objects of this invention will become apparent to those skilled in the art from the reading of the specification and examples which follow.

DESCRIPTION OF PREFERRED EMBODIMENTS

In accordance with this invention the above and other objects are attained with a radiographic element comprising an incorporated developer layer, a radiation sensitive layer comprising (a) a thioether ripened silver halide emulsion precipitated in the presence of a rhodium salt and (b) a stabilizing amount of a polyvalent metal salt, i.e., divalent, trivalent or tetravalent metal salt, and a hydrophilic colloid containing overcoat layer. The thioether-ripened silver halide grains useful in the present invention include those described in U.S. Pat. 3,271,157 issued Sept. 6, 1966 to McBride and those disclosed in U.S. Pat. 3,531,259, issued Sept. 29, 1970 to Wood. The rhodium salt is in the presence of this invention includes rhodium salts including ammonium chlorohydroxide, rhodium chloride, and the like. In addition, still other salts such as K₂RhCl₆, Bi(NO₃)₃·5H₂O; H₂PtCl₆; K₂IrCl₆ and K₂O₂IrCl₆ are effective as are other salts of arsenic, gold, antimony and various mixtures thereof.

The polyvalent metals such as those di-, tri-, and tetravalent metals and their salts which enhance the sensitivity and speed of the silver halide grains include tri- valent antimony, bismuth, arsenic, gold, iridium, rhodium and the like. Tetravalent metal ions include platinum, osmium, iridium and the like. Divalent metal ions include cadmium such as cadmium chloride, cadmium nitrate, and zinc, like zinc nitrate and various manganese salts and the like. The element so-described comprises a support bearing a radiation sensitive layer containing silver halide grains dispersed in a hydrophilic colloid and precipitated in the presence of a rhodium salt, and added to said already formed grains, a stabilizing concentration of a salt of a polyvalent i.e. a di-, tri- or tetravalent metal ion, the improvement comprising employing a coating concentration of from about 350 to about 450 mg./ft.² of said hydrophilic colloid and from 100 to about 200 mg./ft.² of said silver halide. Particularly good results are obtained with a photographic element, and particularly a radiographic element, i.e. one which is radiation sensitive comprising a support bearing a layer comprising a hydrophilic colloid in a concentration from about 350 to about 450 mg./ft.² in which is dispersed a concentration of silver in a coverage i.e. a coating density of less than about 200 mg./ft.² but in a concentration sufficient to provide radiation sensitivity. This improved radiographic element of high image quality comprises a support bearing a high speed, high contrast low silver halide containing layer, said silver halide dispersed in a hydrophilic colloid coated at a density of about 350 to about 450 mg./ft.². By high contrast is meant that value equal to or greater than the difference between the densities of two areas of the sensitive layer after exposure and processing. In the present invention the contrast is about 4 to about 9 and preferably about 4.5 to about 5.5. In a preferred embodiment it has been found that the above described radiographic element provides a high speed, high contrast image in a short time by incorporating in the above described element suitable developing agents.

In yet another embodiment of the present invention there is provided a process for obtaining a high quality radiographic image of a test subject which comprises exposing to a radiation source, said subject in proximate contact, i.e. indirect contact or in close relation therewith, a radiographic element comprising a support bearing a layer comprising a hydrophilic colloid laid down in a coating concentration of from about 350 to about 450 mg./ft.² in which is dispersed a concentration of silver halide in a coating density of less than about 200 mg./ft.², and preferably from about 125 mg./ft.² to about 175 mg./ft.².

In the typical radiographic element designed for medical application, there is generally provided a coarse or large size radiation sensitive silver halide grain such as a silver bromide iodide grain, in order to provide a fast, light sensitive element so that the exposure to radiation is minimized to the patient. From this, one can readily see that the light or energy absorption requirements of this type of radiation-sensitive element is lower, than the type of element customarily used heretofore for industrial radiography. In particular, the industrial radiograph used of element customarily used heretofore for industrial radiography. In particular, the industrial radiograph used heretofore comprises a fine grain silver halide emulsion or layer containing fine grains and, in view of the requirement for absorbing as much X-ray or gamma-ray as possible, the element necessarily contains a very high coating density of silver in order to absorb said radiations. Given these minimal requirements for nondestructive testing, the any other means for improving the sensitivity of the x-ray image, is obvious in that it uses (a) a radiation-sensitive element having coarse silver halide grains typically used for medical radiography and (b) employs said coarse grain in a very light coating density quite unlike heretofore uses elements and processes for industrial radiographs. It is known in the art that by employing paper elements, such as developing paper, printing paper and radiographic paper, it is not possible to utilize extraordinarily high silver coverage, and so when said coverage is reduced, one would normally expect to obtain a dramatic loss of image quality, in view of the fact that the speed is decreased and the D_max, lowered. As will be seen from the examples hereafter quite the contrary results are achieved in the practice of the present invention. The fact that paper radiographs have historically suffered from inferior sensitivity and poor latitude and difficulty in reproducing copies from an original print is borne out in the text, X-rays in Practice, Sproul (1946) McGraw-Hill, pp. 175 et seq. wherein is stated the chief advantage of X-ray paper over film is that of lesser cost. This is the disadvantage of radiographs in that they lack contrast, and that their sensitivity of the flaw detection is poorer than that of film and is likewise borne out in "An assessment of X-ray Papers for Industrial Radiography" Armament Research and Development Establishment, Great Britain, June (1955), Ludgater. Heretofore it has been believed well accepted that
the use of fine grain X-ray film was vastly superior for all purposes and particularly in obtaining image sharpness when compared with photographic paper, substituted for salted paper. Mottle is actually believed to be the combination of various components observed in radiographic elements. For example, quantum mottle, the major contributing factor, results from statistical fluctuations in the spatial distribution of the number of photons in the X-ray image which contribute to the density of the screen structure. The combination of both of these unwanted effects is called screen mottle and they are particularly apparent whenever a fast-image forming system is used and also as the radiation energy is increased, such as in the high exposure time required in industrial radiography.

By the use of term, radiation, it will be understood to mean the transmission of energy through space such as the diffusion or transfer of energy through matter. As applied to the present invention, it relates to the stream of X-rays, gamma-rays and the like of (1) relatively short wave lengths, such as 0.06-2 A. and (2) hard X-rays of shorter wave lengths of higher penetration, i.e., 0.19-0.43 A. and (3) soft X-rays of low penetration having a wave length of from about 11.9 to about 13.6 A.

The silver halide layers and emulsions used with this invention comprise silver chloride, silver bromide, silver bromoiodide, silver chlorobromobromide or mixtures thereof. The emulsions are generally coarse grain, i.e., having a grain size of 0.5-5 μm and can be prepared by any of the well-known procedures, e.g., single jet emulsions, double jet emulsions, such as Lippman emulsions, ammonium emulsions, thiocyanate or thioperoxy ripened emulsions such as those described in Nietz et al. U.S. Pat. 2,222,564 issued Nov. 19, 1940; Illingsworth U.S. Pat. 3,320,060 issued May 16, 1967; and McBride U.S. Pat. 3,271,157 issued Sept. 6, 1966. The silver halide is preferably unfogged and contains at least about 10% bromide, less than about 10% iodide and less than about 50% chloride on a molal basis. Preferably the silver halide is a silver bromoiodide containing about 95% to about 99% bromide, i.e., about 5% to about 1% iodide. Surface image emulsions can be used or internal image emulsions can be used as described Davey et al. U.S. Pat. 2,592,250 issued May 8, 1952; Porter et al. U.S. Pat. 3,206,313 issued Sept. 14, 1965; Berriman U.S. Pat. 3,367,778 issued Feb. 6, 1968; and Bacon et al. U.S. Pat. 3,447,927 issued June 3, 1969. Negative type emulsions can be repalced positively therefor as described in Leemakers U.S. Pat. 2,184,013 issued Dec. 19, 1939; Kendall et al. U.S. Pat. 2,541,472 issued Feb. 13, 1951; Berriman U.S. Pat. 3,367,778 issued Feb. 6, 1968; Schowouenaars British Pat. 723,019 issued Feb. 2, 1955; Illingsworth et al. French Pat. 1,520,821 issued Mar. 4, 1968; Ives U.S. Pat. 2,568,785 issued Aug. 7, 1951; Knott et al. U.S. Pat. 2,456,955 issued Dec. 21, 1948, and Land U.S. Pat. 2,861,885 issued Nov. 25, 1958. The emulsions can be regular grain emulsions such as the type described in Klein and Moisar, J. Phot. Sci., vol. 12, No. 9, September/October 1964, pp. 242-251.

The silver halide layers and emulsions used with this invention can be unwashed or washed to remove soluble salts. In the latter case the soluble salts are removed by chill-setting and leaching or the emulsion can be coagulation washed, e.g., by the procedures described in Hewston et al. U.S. Pat. 2,618,556 issued Nov. 18, 1952; Yackel 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 Walfer et al. U.S. Pat. 2,489,541 issued Nov. 29, 1949.

The photographic layers and 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; Wafer 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. 3,297,448 issued Jan. 10, 1967.

This silver halide layers and emulsions used with this invention can contain speed increasing compounds such as polyvalene glycals, cationic surface active agents and thioethers or combinations of these as described in Piper U.S. Pat. 2,886,437 issued May 12, 1959; Dunn et al. U.S. Patent 3,046,153 issued Nov. 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 radiographic elements of this invention can contain an incorporated developer comprising one or more developing agents such as hydroquinones, catechols, ammophenols, 3-pyrazolidones, ascorbic acid and its derivatives, reductones and phenylene diamines. Combinations of developing agents can be employed as the development 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. 2,588,583 issued Apr. 8, 1952 and Dunn et al., French Pat. 1,505,778.

The radiographic 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, sulfo- nate 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 polysuccinuridic acid diacetyld erbarn and oxoyagum and the like.

The radiographic 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 materials, such as agar, 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 radiographic emulsion layers and 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 synthet-
ic polymeric compounds such as dispersed vinyl compounds such as latex in form and particularly those which increase the dimensional stability of the photographic materials. Suitable synthetic polymers include those described, for example, in Nottor U.S. Pat. 3,142,568 issued July 28, 1964; White U.S. Pat. 3,193,836 issued June 7, 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, 1963; Ream et al. U.S. Pat. 3,287,389 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 methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, those which have crosslinking sites which facilitate hardening or curing, those having recurring sulfonate units as described in Dykstra Canadian Pat. 774,054.

The radiographic 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. Patent 3,206,312 issued Sept. 14, 1965 or insoluble inorganic salts such as those described in Trecov U.S. Pat. 3,428,451 issued Feb. 18, 1969.

The radiographic layers employed in the practice of this invention can contain plasticizers and lubricants such as polyethylene glycols, silicones, and diols of the type described in Milton et al., U.S. Patent 2,960,404 issued Nov. 1, 1966; fatty acids or esters such as those described in Robjins 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 Patent 955,061 issued Apr. 15, 1964.

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

The radiographic 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. 2,592,101 issued July 11, 1961 and Lynn U.S. Pat. 2,929,655 issued Feb. 1, 1955.

The radiographic 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 Patent 92,067 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 Jensen German Patent 1,150,274, Oetiker et al., U.S. Patent 3,406,070 issued Oct. 15, 1968 and Heilbr New Zealand Patent 1,530,244.

Spectral sensitizing dyes can be used conveniently to confer additional sensitivity to the radiation sensitive silver halide emulsion of the radiographic elements of the invention. For instance, additional spectral sensitization can be obtained by treating the emulsion with a solution of a sensitizing dye in anorganic solvent or the dye can be added in the form of a dispersion as described in Owens et al. British Patent 1,154,781 issued June 11, 1909. For optimum results, the dye is either added to the emulsion as a final step or at some earlier stage.

Sensitizing dyes used 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. Patent 2,503,776 issued Apr. 11, 1950; Brooker et al. U.S. Patent 2,493,748 issued Jan. 10, 1950; and Tuber et al. U.S. Patent 3,384,486 issued May 21, 1968. Spectral sensitizers which can be used include the cyanines, merocyanines, complex (tri or tetra-}

nuclear) merocyanines, complex (tri or tetracyan) cyanines, holopolar cyanines, styryls, hemicyanines (e.g. enamine hemicyanines), oxonols and heminoxonols.

Dyes of the cyanine classes can contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazines, thiazolamines, semiazolones and imidazolones. Such nuclei can contain alkyl, alkenyl, hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminoalkyl and enamine groups and can be fused to carbocyclic or heterocyclic ring systems either unsubstituted or substituted with halogen, phenyl, alkyl, alkoxyalkyl, cyano, or alkoxy groups. The dyes can be symmetrical or unsymmetrical and can contain alkyl, phenyl, enamine or heterocyclic substituents on the methine or polyethylene chain.

The merocyanine dyes can contain the basic nuclei mentioned above as well as acid nuclei such as thiodyantoinos, rhodamines, oxazolenediones, thiazolenediones, barbituric acids, thiazolineones, and malononitrile. These acid nuclei can be substituted with alkyl, alkenyl, phenyl, carboxyalkyl, sulfoalkyl, hydroxyalkyl, alkoxyalkyl, alkymino groups, or heterocyclic nuclei. Combinations of these days 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. Patent 2,933,390 issued Apr. 19, 1960, and Jones et al., U.S. Patent 2,937,059 issued July 31, 1960.

The various layers, including the radiographic layers, employed in the practice of this invention can contain light absorbing materials and filter dyes such as those described in Sawday U.S. Patent 2,523,921 issued May 31, 1966; Gasparr U.S. Patent 2,274,782 issued Mar. 3, 1942; Silverstein et al., U.S. Patent 2,527,583 issued Oct. 31, 1950, and VanCampen U.S. Patent 2,956,879 issued Oct. 18, 1960. If desired, these dyes can be mordanted, for example, as described in Miller et al., U.S. Patent 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. Patent 2,912,343 issued Nov. 10, 1959; McCrosen et al., U.S. Patent 3,342,605 issued Sept. 19, 1967; Audran U.S. Patent 2,996,287 issued Aug. 15, 1961 and Johnson et al., U.S. Patent 3,425,835 issued Feb. 4, 1969.

The radiographic 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. Patent 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. Patent 2,761,791 issued Sept. 4, 1956 and Wynn British Patent 837,095. This invention also can be used for silver halide layers coated by vacuum evaporation as described in British Patent 968,453 and LuValle et al., U.S. Patent 3,219,451 issued Nov. 23, 1965.

This invention can be used with elements designed for color photography, for example, elements containing color-forming couples such as those described in Frohlich et al., U.S. Patent 2,376,679 issued May 22, 1945; Jelley et al., U.S. Patent 2,322,027 issued June 15, 1943; Fierke et al., U.S. Patent 2,801,171 issued July 30, 1957; Godowsky U.S. Patent 2,698,794 issued Jan. 4, 1955; Barr et al., U.S. Patent 3,227,534 issued Jan. 4, 1966; and Graham et al., U.S. Patent 3,046,129 issued July 24, 1962; or elements to be developed in solutions containing color-forming couples such as those described in Manners et al., U.S. Patent 2,252,718 issued Aug. 19, 1941; Carroll et al., U.S. Patent 2,592,243 issued Apr. 18, 1952; and Schwan et al., U.S. Patent 2,950,970 issued Aug. 30, 1966; and in false-sensitized color materials such as those described in Hanson U.S. Patent 2,763,549 issued Sept. 18, 1956.
Radiographic 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, amino-phenols, 3-pyrazolidones, phenylendiamines, ascorbic acid derivatives, hydroxylamines, hydrazines, reductones and the like; web processing as described in Tre-gilus et al. U.S. Pat. 3,179,517 issued Apr. 20, 1963; stabilizing the processing as described in Russell et al. "Stab-ilization Processing of Films and Papers," P.S.A. Journal, vol. 16B, August 1950; monobath processing as described in Levy "Combined Development and Fixation of Photo-graphic Images with Monobaths," Phot. Sci. and Eng., vol. 2, No. 3, October 1958, and Barnes et al. U.S. Pat. 3,922,019 Dec. 7, 1974, and July 16, 1974. 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 applica- tion processing as described in Example 3 of Kitae U.S. Pat. 3,418,132 issued Dec. 24, 1968.


This invention can be used in elements designed for physical development such as those described in Agfa British Pat. 920,277 and Gilman et al. British Pat. 1,131,238.

Hydrophilic colloid materials which can be used in the practice of the invention include various water-permeable binder vehicles which materials can be sus-pended in colloidal dispersions. Hydrophilic colloidals suit- able as binder vehicles and layers include proteinaceous compounds such as, for example, gelatin, colloidal albumin and other hydrophilic colloids such as, for example, polyvinyl compounds, cellulose derivatives, acrylamide polymers, etc., though gelatin materials are preferred.

The high molecular weight materials for binder vehicles and layers which are generally considered soluble in aque- ous solutions form small discrete particles when mixed with an aqueous gelatin emulsion, as may be determined upon observation of a photomicrograph, can be considered hydrophilic colloids for purposes of this invention.

The phosphors in the X-ray intensifying screens possess the characteristic of having a substantial part, that is, more than half, of their total spectral emission at less than about 410 nm. This emission is substantially in the ultra-violet range of the spectrum and it has been found that a host matrix comprising at least one of certain heavy metal phosphors are particularly useful therefor. Such phosphors have a physical density greater than at least about 2.5 and a ratio of refractive index to metal density greater than 3.9. However, particularly effective novel combinations in the practice of this invention use heavy metal phosphors, including those made from the lanthanide group of the periodic table. The latter rare earth elements have an atomic number in the range of between 58 to 71 and include lanthanum, cerium, samarium, gadolinium, holmium, erbium and thulium. Effective heavy metal phosphors are those such as lanthanide- or lead-activated BaSO₄ and BaBr₂SO₄, lead-activated barium sili-cates, gadolinium-activated yttrium oxide, and barium fluoride, barium fluoride chloride and the like. Said phosphors can be further activated by rare earth activators alone and in combination. These phosphors can be pre- pared by a number of ways, such as set forth in Belgian Pat. 703,998 issued Mar. 18, 1969 to Luckey; in Buchan et al. J. Applied Physics, vol. 39, pp. 4342-4347 (1968) and in Clapp and Ginnier, L., of the Optical Soc. of America, vol. 37, No. 1, pp. 355-62 (1947). These phosphors can be used in screens which are either integral or non-integral with radiographic image forming elements which elements have single coated light sensitive layers.

A preferred use of the radiographic elements necessary to the invention herein is in combination with radiographic intensifying screens particularly because of the range of the X-rays by the phosphor host is so high. In fact, the absorption of X-ray energy by the radiographic screens comprising certain phosphors is so high that single sided radiographic systems can be employed which systems form part of the present invention. These single sided radiographic systems provide such extraordinary sharpness and high speed that they are equal or superior to similar results obtained by conventional double-sided systems. Among the various phosphors exhibiting the desirable luminescence is the terbium-activated lanthanum oxysul- fate which has a negligible afterglow and whose green emission makes it particularly suitable for fluoroscopic and radiographic application.

The intensifying fluorescent screens, which can form part of the radiographic element of our invention, consist essentially of phosphors which can be dispersed or sus-pended in a suitable binder such as those set forth in U.S. Pat. 3,300,310 and 3,300,311 supra. which employ a water-soluble polymer of alkylacrylate and acrylic acid, copolymers of vinyl chloride and vinyl acrylate, polyvinyl butyral as set forth in German Pat. 1,186,332 issued Jan. 28, 1963, to Patten et al., a copolymer of molecular polymer binder such as resins, polymers or copolymers of polycarbonate which comprise recurring carbonate units in the polymer chain, and the like, polymers of acrylic acid esters containing small percentages of a chlorine-containing derivative, such as acrylonitrile copolymers such as Hycar (a trademark of B.F. Good-rich Chemical Company for the thus-described dry rubber polymers). Among preferred binders are those screening-binders including blends of copolymers of ethyl acrylate, chloro ethyl vinyl ether with a poly alkyl methacrylate and polyurethane elastomers. The phosphors can be present in the binder in a wide variety of ratios such as, for example, from about 30:1 to about 4:1 and preferably in the range of about 16:1 to about 6:1. The coverage of the phosphor can vary over a wide range. Effective coverage can be determined through experimentation. A preferred coverage of said phosphors is in the range of about 15 to about 150 grams/m². With respect to general purpose screens good results are achieved with a coverage in the range of about 50 to 110 grams/m² and with re-spect to high definition screens a coverage of from about 15 to 35 grams/m² yields good results. Likewise, these screens can be coated in a variety of ways such as di-rectly over the photographic layer or on both sides of a double coated or single coated element. Intermediate
layers, such as stripping layers, protective or overcoat layers, can likewise be employed between or over the X-ray emulsion layer and the intensifying screen. Said layers may comprise hydrophilic colloid material such as gelatin, gelatin derivatives, cellulose esters, alkyd acrylate-containing polymers and the like.

The radiographic elements of our invention employ, in addition to the phosphor-containing intensifying screen, a suitably supported image recording layer such as one comprising silver halide as disclosed hereinbefore. The radiographic elements and combinations so described can be constructed such that the photographic elements are either separate, i.e. non-integral or integral, i.e. as a separate distinct layer of an element comprising a silver halide emulsion coated onto a support with the intensifying screen. Said silver halide can be present in a layer or coating such as a single coating on one side of a support. Suitable supports are those having the properties to permit their ready passage through a rapid automatic processor if desired. Said support should, therefore, be reasonably flexible and preferably able to maintain the dimensional stability and integrity of the various coatings thereon. Typical supports are fibrous materials used as supports such as cards or paper which are coated with α-olefin polymers, particularly polymers of α-olefins containing two to ten carbon atoms, as exemplified by polyethylene, polypropylene, ethylene-butene copolymers, and the like. In addition, if desired, said supports can comprise light absorbent materials either within the support itself, on a layer over and/or under said support, or both.

The thickness of said support can vary as is well-known in the art in order to practice effectively our invention. The silver halide can comprise varying amounts of silver chloride, silver iodide, silver bromide, silver chlorobromide, silver bromoiodide and the like. Particularly good results are obtained with gelatin silver bromoiodide emulsions in which the average grain size of the silver bromoiodide crystals is in the range of about 0.5 to about 5 microns. These layers are applied by means well-known in the art.

The photographic silver halide coatings can also contain additional additives, particularly those known to be beneficial in photographic emulsions. For example, they can contain speed-increasing compounds, for example, "onium" salts, such as quaternary ammonium or tertiary sulfonium salts, polyalkylene glycols, thioureas and the like. The photographic silver halide coatings can be stabilized with mercury compounds, azaindazoles, quaternary benzothiazolium compounds, hydroxy substituted aromatic compounds, and the like.

The photographic silver halide elements which are part of the radiographic combinations described herein provide very good results in image sharpness without absolute need for any dyes or other light absorbing materials. While there is no need for employing dyes or other light absorbing materials in either the film, the screen, or both, extraordinary results can be obtained by using such dyes and light absorbing materials. Where used, light absorbing dyes and light absorbing materials can be in the emulsion layer or in an auxiliary layer such as a layer coated between the support and the emulsion layer, or the light absorbing dyes and materials can be included in both the emulsion and the auxiliary layer. These elements can also contain inert particles such as those often employed as matting agents in photographic emulsions. Suitable materials, for example, include carbon dioxide, glass, starch, polyethylene methacrylate and the like. Such inert particles are often included in an emulsion layer alone and in combination.

These elements can likewise contain various protective overcoats such as those which comprise colloidal silica in an overcoat comprising gelatin and at least another hydrophilic colloid, including gelatin-compatible acrylic polymers which improve various physical characteristics and optical clarity.

Processing can be effected not only by utilizing the incorporated developer system but also in a variety of other ways including the multi-tank manual methods but preferably in a unidirectional, multi-roller high speed processing apparatus described in Belgian Patent 700,301 issued Aug. 31, 1967, to Barnes et al. These processes can be effected and the combinations of this invention can be processed respectively according to U.S. Patent 3,232,761 issued Feb. 1, 1966, to Allen and Burns; Res. 10 issue 26,601.

The silver-containing film-screen combinations of our invention can likewise be used with unexpectedly good radiographic results in solvent transfer systems such as where single and double coatings are employed. In addition where positive images are so obtained they are easily converted to negative microfilm images either during or after processing. Equally good results are obtained when these novel combinations contain color couplers, such as those described in British Patent 799,588 issued Aug. 13, 1958, to Whitmore and Elinos, and by using these novel combinations and processes in color film-containing systems.

As a result of our novel phosphors and screens containing them, radiographic combinations are used effectively in recording X-ray images and thus utilized to provide widespread film-screen combinations having improved sharpness, and with vastly increased speed. EXAMPLE 1

A typical coarse-grained, silver bromoiodide (99:1) emulsion suitable for use in X-ray film elements is prepared by employing the "double-jet" technique. An aqueous solution of potassium bromide and potassium iodide and another aqueous solution of silver nitrate are added simultaneously over a period of 10 minutes to an aqueous gelatin solution at 65.6° C. A thioester ripening agent, 1,8-dihydroxy-3,6-dithiocane (10.9 g./mole Ag) is added to the precipitated emulsion which is then digested for approximately 30 minutes, salt coagulated, washed thoroughly, dispersed and sulfur and gold sensitized. The chemically sensitized emulsion is combined with the following solutions:

Amp. /1.14 moles Ag ml.
Methanol solution containing 0.1% by weight anhydro -5.6 dichloro-1,3'-diethyl-3-(3-sulfoaryl)benzimidazolooxocarboxycyanine hydroxide

Aqueous solution containing 0.67% by weight 4-hydroxy -6 -methyl-1,3,3a,7-tetraazidindene sodium salt

Aqueous solution containing 2.8% by weight p-tocopheryl-5-ethylquinoline-ethyl sodium sulfonate

This photosensitive composition is mixed thoroughly and then coated at 120 mg. Ag/ft² and 204 mg. gelatin/ft² over an incorporated developer layer which originated from a composition containing the following compounds and solutions:

Amp./1.14 moles Ag ml.
Gelatin

Aqueous solution containing 4.6% by weight glutaraldehyde di-sodium bisulfite and 6.2% by weight methyl hydroquinone 5 liters...

Aqueous methanol solution containing 33.5% by weight methanol, 2.16% by weight 5,5-dimethyl-1,3-cyclohexanedicarboxlic acid, 2.0% by weight 1-phenyl-3-pyrazolodine and 0.27% by weight 5-nitro-1H-indazole 100.00

The bottom layer is coated on paper support at 6.90 g. solution/ft², therefore resulting in an incorporated developer layer containing approximately 222 mg. gelatin/ft², 76 mg. methyl hydroquinone/ft² and 15 mg. 1-phenyl-3-pyrazolodine/ft².
The radiographic element is then overcoated with a gelatin containing composition at 5.85 g. solution/ft.², thereby resulting in a layer containing approximately 53 mg. gelatin/ft.². The dried multilayer radiographic element is exposed to X-ray radiation (110 kv., 10 ma.) for 15 seconds at a distance of 3 feet and then processed by passing the exposed element through an Eastman Kodak Ekktometric Processor which activates the incorporated developer element and stabilizes it. The processed element is assigned a relative speed of 100 and is equal in speed to Eastman Kodak Industrial X-Ray Film, Type M which has been exposed in the same manner and processed in an Elton-hydroquinone developer for 5 min. at 20° C.

EXAMPLE 2

A coarse-grained silver bromoiodide (99:1) emulsion is prepared according to the procedure described in Example 1 except that the precipitation is carried out in the presence of 0.01 mg. ammonium chloride/mole Ag. After the digestion step (30 min.), which is carried out in the presence of the above-described thioether ripening agent, the emulsion is salt coagulated, washed thoroughly, redispersed, sulfur and gold sensitized and then stabilized by the addition of a cadmium salt as shown below.

Amp./.14.14 mles Ag., Ml. Aqueous solution containing 5.67% by weight 4-hydroxy-6-methyl-1,3,3a,7-tetrahydrodien sodium salt 75.0 Aqueous solution containing 30.5% by weight cadmium bromide 200.0 Polyacrylamide 200.0 Aqueous solution containing 2.8% by weight p-1-octylphenoxyethoxyethyl sodium sulfonate spreading agent 10.0

and coated with 403 mg. gelatin and 150 mg. Ag/ft.² over an incorporated developer layer which originated from a composition containing the following compounds and solutions:

Gelatin 908 Aqueous solution containing 6.43% by weight sodium formaldehyde bisulfite, 3.38% by weight hydroquinone and 3.0% by weight methyl hydroquinone ------- 4.2

Aqueous methanol solution containing 1.0% by weight 1-pyrazolidone, 0.28% by weight 5-nitro-1H-indazole and 66.8% methanol ------- 2.0

The incorporated developer contains approximately 330 mg. gelatin/ft.², 51.6 mg. hydroquinone/ft.², 46.1 mg. methyl hydroquinone and 7.3 mg. 1-phenyl-3-pyrazolidone/ft.². The radiographic element is then overcoated with a gelatin-containing composition at 5.85 g. solution/ft.², thereby resulting in a protective layer containing approximately 53 mg. gelatin/ft.². The dried radiographic element is exposed and processed as described in Example 1. In comparison with Example 1, the processed element has a relative speed of 150; the images keep satisfactorily for several weeks, and the processed element can be handled readily for image evaluation.

EXAMPLE 3

The photographic elements described in previous Example 2 and in U.S. Patent 3,488,709 issued to Sidebotham Jan. 6, 1970, are radiographically exposed and then processed in the same manner as described in Example 2. These elements are compared with the following results:

- Contrast: Example 1 = 1
- Density: Example 1 = 1
- Quantum motio: Example 1 = 1
- Speed: Example 1 = 1
- Hydrophilic colloid: Example 1 = 208
- Hydrophilic colloid: Example 2 = 403

Ratings: 1=highest, acceptable; 2=moderate; 3=low; and 4=lowest, unsatisfactory.

The speed of the present element is determined and compared to the speed of Kodak Industrial Radiographic Film Type AA. The former has a speed of 610 and the latter 100. ASA speed is calculated from the customarily used formula

\[ E = \frac{10^{13}}{B} \]

At an exposure of 100 microsecond to white light, the ASA value is about 8000, of the present element.

EXAMPLE 4

Employing a non-integral lead foil Du Pont Industrial Type luminescent screen, comparative tests are conducted on processed Eastman Kodak Industrial X-Ray Film Type M, an extra fine grain emulsion of high contrast but not thioether ripened emulsion and the radiographic element of the present invention after exposure. Processing is accomplished for M Type film in an Elton-hydroquinone developer for 5 minutes at 20° C. in order to obtain optimum speed. The present element is processed utilizing its incorporated developer system and the speed comparisons indicate a 60 fold increase in speed of the paper element of the invention over the Type M film. The mottle and physical characteristics of the present element is likewise superior. The exposure is made against various aluminum castings and a honeycombed stainless steel grid to determine the presence of latent defects. Of the fractures discovered, the prior art film could only show those of a gross nature and in poor contrast while the present element showed various undetected hairline fractures in addition thereto and with considerably good contrast. Equally good results are obtained in the process of recording a radiographic image by employing a variety of luminescent phosphor screens comprising the heavy metal ion and an activator element, e.g., (1) europium activated barium lead sulfate, (2) europium activated gadolinium oxide, (3) and terbium activated lanthanum oxysulfide. All are prepared according to the process described in Belgian Patent 703,998 issued Mar. 18, 1969, to Luckey and are dispersed in a suitable binder comprising a blend of copolymers of ethyl acrylate, chloroethyl vinyl ether with a poly(alkyl methacrylate) in a coating coverage of about 14.1 parts of pigment, i.e., phosphor, to binder.

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 element comprising an opaque paper support coated with a radiation sensitive layer comprising from about 350 to about 450 mg./ft.² of a hydrophilic colloid and from about 100 to about 200 mg./ft.² of silver halide grains precipitated in the presence of a rhodium salt and thioether ripened, and, added to said grains, a stabilizing concentration of a salt of a polycyclic metal ion and a luminescent screen comprising a heavy metal containing luminescent phosphor.

2. The element of claim 1 further comprising one or more silver halide developing agents.

3. The element of claim 1 in which said paper support is resin coated.

4. The element of claim 1 in which said hydrophilic colloid is gelatin.
5. The film screen combination of claim 1 in which said screen is integrally combined with said film.

6. The element of claim 1 in which said silver halide is present as coarse grains of silver bromoiodide.

7. A process for obtaining a high quality radiographic image of a subject which comprises exposing to X-rays or gamma-rays said subject in proximate contact with a radiographic element comprising an opaque paper support, a radiation sensitive layer comprising a hydrophilic colloid in a coating concentration of from about 350 to about 400 mg./ft.² in which is dispersed a radiation-sensitive amount of silver halide in a coverage of from about 100 to about 200 mg./ft.², said silver halide precipitated in the presence of a rhodium salt thioether ripened and added to said grains, a stabilizing concentration of a salt of a polyvalent metal ion.

8. The process of claim 7 in which said element further comprises one or more silver halide developing agents.