May 22, 1973

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22 Claims

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3,734,735 COLOUR RADIOGRAPHY Jacques Elie Bories, La Varenne St. Hilaire, France, as-signor to Agfa-Gevaert N.V., Mortsel, Belgium Filed Aug. 22, 1969, Ser. No. 852,246 Int. Cl. G03c 7/00

U.S. Cl. 96-55

ABSTRACT OF THE DISCLOSURE

X-ray recording method using photographic material having at least one silver halide emulsion layer and each such layer on color development gives a monochromatic blue dye image. Exposure can be directly to an X-ray image or indirectly by way of fluorescent screens and the 15 like. The blue dye image absorbs strongly in the red spectral region and at least 30% as much in the green spectral region and can be produced by a mixture of color couplers for cyan and magenta. If plural emulsion layers are used, the same color coupler or mixture of color cou- 20 plers is provided in each layer to give an identical monochromatic blue dye image. The photographic materials per se are also disclosed.

25This invention relates to improvements in radiography and photosensitive recording materials suited therefor.

In common radiography the radiation pattern, emerging from the radiographed object is transformed into a twodimensional image.

Methods for increasing the information content of this image by the use of certain colour photographic materials have already been described (see e.g. the survey of colour radiography by Dr.-Ing. H. V. Richter and Prüf.-Ing. D. Linke in the article: "Grundlagen und Verfahren der 35 Color-Radiografie," Die Technik, vol. 21, No. 7/66, pages 424-431).

The use of multi-colour recording materials makes it possible to visually retrieve more information from the recorded colour image than from a corresponding black- 40 and-white image since the latter only provides differences in brightness while a multicolour image offers in addition thereto differences in hue and saturation.

Because the production of a multicolour radiographic image is based on rather sophisticated combinations of 45 light-sensitive silver halide emulsion layers, exposure and processing techniques, it would be interesting to introduce a simplification by producing a monochromic image, optionally together with a silver image, and to have available an easy visual retrieval of more information than 50contained in a corresponding black-and-white image. Further it would be interesting to dispose of radiation-sensitive colour developable silver halide photographic materials the sensitivity of which is sufficiently high to allow the substitution of black-and-white silver halide materials 55 commonly used with fluorescent tungstate screens.

It is an object of the present invention to provide a process including a radiographic exposure, a development of a monochromic colour image and an improved visual retrieval of information.

It is another object of the present invention to provide photographic silver halide materials of low as well as of high photosensitivity by means of which monochromic radiographic images are obtained offering a larger infor-65mation content on visual inspection with white light than commonly produced black-and-white silver image radiographs can.

More particularly it is an object of the present invention to provide photographic silver halide materials for use in $_{70}$ radiography containing in (a) silver halide emulsion layer(s) a colour coupler or mixture of colour couplers

for producing a monochromic image. These materials for this use are equivalent to conventional black-andwhite silver halide photographic materials as far as photosensitivity and ease of processing are concerned, but by visual inspection of the monochromic image are capable to provide a larger retrieval of information originally contained in the incoming radiation pattern than is possible to obtain from a black-and-white silver image produced with conventional black-and-white radiographic materials under the same exposure and normal black-and-white processing conditions.

It is a further object according to some of the embodiments of the present invention to economize on the silver halide content of radiographic materials and to produce dye images which in respect to silver images have a less grainy structure and therefore yield improved definition.

The invention is not limited to these objects and other objects and advantages can be learned from the following description and examples.

A process has now been found including recording and visual retrieval of information provided in the form of penetrating radiation characterized by the steps of:

(1) directly or indirectly recording said penetrating radiation as (a) developable latent silver image(s) in a photographic silver halide material, which material contains at least at the moment of the development, a substance or substances that with the aid of the exposed silver halide and possibly by reaction with (an) other substance(s) so-called oxidized colour developing agent(s) is(are) capable to form in said material by means of one or more silver halide emulsion layers a monochromic image mainly absorbing in two primary colour spectral regions, preferably the red and green,

(2) developing the recorded latent image(s) by means of (a) reducing substance(s) that produce(s) (a) silver image(s) together with said monochromic image by oxidation in situ or by oxidative coupling with (a) colour coupling agent(s), so-called colour coupler(s), and

(3) inspecting the obtained monochrome image, after optional removal of the silver image(s), with white light, and optionally inspecting it with coloured light the spectral composition of which is such that it is modulated by the monochromic image, e.g. inspection with yellow or red light in case the dye image absorbs or modulates red and green light.

Preferably the spectral absorption of the monochromic image takes place in two primary colour spectral regions laying within the spectral wavelength range of 500 to 700 nm.

According to a specially preferred embodiment the spectrum of the monochromic image together with the silver image (not-bleached) has an absorption maximum situated between 660 nm. and 580 nm. and the spectral density of the dye and silver image taken together is at 540 nm., preferably at least 30% of the maximum of the absorption being situated in the region of 660-600 nm.

By the wording "directly or indirectly recording in-visible penetrating radiation" is meant that the present invention includes photographic recording based on the direct action of ionizing radiation such as X-rays, alpha, beta or gamma rays and photographic processes based on the action of secondarily produced energetic ionizing particles, e.g. electrons or electromagnetic radiation, e.g. visible light or ultra-violet light modulated according to a pattern or signals of penetrating radiation including neutrons. The recording includes all types of exposure with radiation that produces a latent silver image, e.g. simultaneous exposure to a pattern of such radiation. and also scanning-wise exposure e.g. by means of a light spot that is modulated according to the radiographic information to be recorded. Electronic image-intensifying

systems can be applied to improve the brightness of the image before its photographic recording.

A colour-developable silver halide photographic material suited for use in radiography and visual retrievel of information according to the present invention comprises at least one silver halide emulsion, which contains a substance producing oxidatively a dye, e.g. a leuko dye oxidizable to a dye with exposed silver halide or a colour coupler or mixture of colour couplers by means of which on colour development a dye image is formed that ab-10 sorbs in at least one primary colour region and for at least 30% in respect to said region in another primary colour region of the visible spectrum. Best results in optical retrieval of information with the normal human eye seems to be obtainable with a monochromic dye image mainly 15absorbing in the red region of the visible spectrum and absorbing in the green region for at least 30% in respect of the red region in other words cyan images with a fairly large side-absorption in the green and blue dye images are preferred.

According to a preferred embodiment of the present ²⁰ invention a photographic material is used that contains at least one silver halide emulsion layer containing a substance producing on development by oxidation a dye or containing a colour coupler or mixture of colour 25 couplers by means of which on colour development in said emulsion layer a dye image is formed which absorbs in the red (700-600 nm.) and green (600-500 nm.) region of the spectrum, and which in the blue region (400-500 nm.) at 450 nm. has a spectral absorption not higher than 30 its maximum absorption in the green region of the spectrum.

Preferably the photographic silver halide emulsion(s) used in the present invention, at least at the stage of the development contain(s) a colour coupler that forms a 35 dye with the oxidation product of an aromatic primary amino developing agent, e.g. of the p-phenylenediamine type, which dye absorbs in at least one primary colour region of the visible spectrum and absorbs for at least 30% in respect to said region in another primary colour 40region, and contain(s) an amount of silver halide not higher than is necessary for obtaining a maximum-silverimage-density of 2.00 when said silver image is formed under the developing conditions applied for obtaining a maximum colour density at the wavelength of maximum 45 H₃C-(CH₃)₁₂-CH=CH-CH₂-CH-CONHspectral absorption of the dye image.

More preferably phenol or α -naphthol type colour couplers are used that on colour development of the exposed silver halide with an aromatic primary amino developing agent form a quinonimine dye mainly absorbing in red and green and having an absorption maximum in the spectral wavelength range of 700 to 550 nm. When a mainly blue dye is produced by means of one and the same colour coupler a marked economy in silver halide consumption is obtained in respect of the use of a magenta 55 forming colour coupler in one silver halide emulsion layer and a cyan forming colour coupler in another silver halide emulsion layer and in respect of the use of a mixture of a magenta forming colour coupler and a cyan forming colour coupler in one and the same emulsion layer.

In order to further reduce the consumption of silver halide preferably so-called 2-equivalent couplers can be used that need only 2 instead of 4 molecules of exposed silver halide for the production of 1 dye molecule. Such couplers contain in the coupling position e.g. a halogen atom such as iodine, bromine or chlorine (see for such type of couplers e.g. the U.S. patent specification 3,006,759 of Anthony Loria, Warren A. Reckhow and Ilmari F. Salminen, issued Oct. 31, 1961).

Particularly suited phenol or α -naphthol type colour 70 couplers are those that on development of the exposed silver halide with an aromatic primary amino developing agent, e.g. of the p-phenylene-diamine type, form a quinoneimine dye having its absorption maximum in the range of 570 to 660 nm,

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Phenol couplers having such properties correspond, e.g., to the following general formula:



wherein: R represents a carboxylic acid acyl or sulphonic acid acyl group including said groups in substituted state, e.g., an aliphatic carboxylic acid acyl group, an aromatic carboxylic acid acyl group, an heterocyclic carboxylic acid acyl group, e.g. a 2-furoyl group or a 2-thienoyl group, an aliphatic sulphonic acid acyl group, an aromatic sulphonic acid acyl group, a sulphonyl thienyl group, an aryloxy-substituted aliphatic carboxylic acid acyl group, a phenyl carbamyl aliphatic carboxylic acid acyl group, or a tolyl carboxylic acid acyl group.

For such type of colour couplers and their preparation we refer e.g. to the U.S. Patent Specifications 2,772,162 of Ilmari F. Salminen and Charles R. Barr, issued Nov. 27, 1956 and 3,222,176 of Jan Jaeken, issued Dec. 7, 1965, and to the United Kingdom patent specification 975,773, filed Sept. 4, 1961 by Gevaert Photo-Producten N.V.

When known cyan-forming and magenta-forming couplers are used in separate silver halide emulsion layers and/or in admixture in one and the same silver halide emulsion layer, blue, reddish-blue to greenish-blue monochrome images can be obtained by means of p-phenylenediamine developing agents.

For that purpose α -naphthol and phenol type couplers employed in the subtractive colour photographic system for producing the cyan image, and pyrazolone, oxindole and indazolone type couplers for producing the magenta image can be applied.

The colour couplers are preferably applied in the emulsion layer(s) in diffusion-resistant state but can also be applied in dissolved state from the developing bath.

The following phenol colour couplers are suited for application according to the present invention.



melting point: 134° C. (preparation as described in Example 1).

50 (2)

a



melting point: 98° C. (see preparation 3 of the United States patent specification 3,222,176 as mentioned above.)



melting point: 115° C. (see preparation 5 of the U.S. Pat. specification 3,222,176 as mentioned above).



75 melting point: 146° C. (see preparation 2 of the United

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Kingdom patent specification 975,773 as mentioned above).

The colour couplers 2, 3 and 4 are preferably coupled with p-phenylenediamine in order to yield a dye absorbing in the red and to a large extent absorbing in the green.

The colour coupler 1 is preferably coupled with N-hydroxyethyl-N-ethyl-p-phenylenediamine.

Other colour coupling systems do not necessarily involve the presence of a colour coupler and colour developing agent. Thus, in the present invention also such 10 colour-forming systems can be applied in which a compound by simple oxidation with the exposed silver halide produces a coloured substance in situ. In that respect reference is made, e.g., to P. Glafkides, Photographic Chemistry, vol. II, Fountain Press, London (1960) p. 603–605. 15 More particularly reference is made to the colour development according to Homolka, in which leuke indigo derivatives are used. Indoxyl and thioindoxyl are oxidized to the blue indigo and the magenta thioindigo respectively.

Preferred colour developing agents for use in combi-20 nation with phenol, α -naphthol, pyrazolone and indazolone type colour couplers are N,N-dialkyl-p-phenylenediamines and derivatives thereof, e.g. N,N-dimethyl-pphenylenediamine, N-butyl-N-sulphobutyl-p-phenylenediamine, 2-amino-5-diethylaminotoluene hydrochloride and 25 4-amino - N - ethyl-N(β -methane sulphonamidoethyl)-mtoluidine sesquisulphate monohydrate or N-hydroxyethyl-N-ethyl-p-phenylenediamine.

In rapid processing preferably N-butyl-N-sulphobutyl-pphenylenediamine or N-hydroxyethyl-N-ethyl-p-phenyl- 30 enediamine are used.

Different types of silver halide, e.g. silver chloride, silver bromide, silver chlorobromide, silver chlorobromoiodide, silver chloroiodide and silver bromoiodide can be employed. Iodide-containing bromide emulsions, preferably containing up to 10 mole percent of iodide are especially useful for directly or indirectly recording penetrating radiation in the form of a monochromic image according to the present invention.

In order to obtain radiographic silver halide materials 40 that are suited for colour development with p-phenylenediamine colour developing agents and that have a photosensitivity of practically the same value as commercial black-and-white developed radiographic material suited for exposure with the aid of fluorescent tungstate screens 45 have, an amount of silver halide (preferably silver bromide-iodide containing from 10 to 2 mole percent of iodide) corresponding with 5 to 16 g. of silver nitrate per sq. m. is present in the photographic materials. Preferably for obtaining a very good modulation transfer characteristic an amount of silver halide corresponding with 6 to 12 g. of silver nitrate per sq. m. is present.

The colloid binder of the silver halide preferably essentially consists of gelatin, and preferably is present in an amount of 3 to 7 g. per sq. m. in a single silver halide 55emulsion layer.

According to the present invention colour materials yielding a dye image combined with a silver image having a low Callier factor are produced. The Callier factor is the quotient:

specular density diffuse density

(see Fundamentals of Photographic Theory by T. H. James and George C. Higgins (1960), Morgan and $_{65}$ Morgan Inc., New York, p. 190).

Preferably the radiographic materials suited for use according to the present invention contain a colour coupler or mixture of colour couplers suited for copulation with an oxidized p-phenylenediamine type developing agent and an amount of silver halide in an excess of 50 to 150% in respect to the equivalent amount necessary in the dye forming reaction using exposed silver halide and a colour developing agent of the p-phenylenediamine type. The ratio of the maximum densities (Dr.Dr.) is the yiend are

spectrum range built up by the monochromic dye image (maximum spectral density D_1) and by the silver image(s) (maximum density D_2 under white light viewing conditions) is preferably between 1:1 and 5:1 and is more preferably smaller than 3:1. The gamma is the straight line portion of the sensitometric curve of the monochromic dye image measured at maximum spectral absorption is preferably from 1.5 to 4.

According to a specially preferred embodiment the radiographic material used according to the present invention, contains on both sides of a transparent support, e.g. a transparent resin support a silver halide emulsion layer comprising (a) colour coupler(s) for producing a monochromic dye image as described herein.

The radiation-sensitivity of film coated on one side as well as of film coated on both sides with a silver halide emulsion layer can be more effectively used when socalled intensifying screens are applied.

Indeed, the degree of photographic effect of the gamma or X-rays depends upon the amount of radiation energy absorbed by the silver halide emulsion coating(s) of the film; this is some 1% for radiation of medium penetrating power. The remaining radiation passes through the film and consequently is not used. In order to remedy this, the film is sandwiched between two intensifying screens. Under the action of the gamma or X-rays these screens either fluoresce (fluorescent and intensifying screens) or emit electrons (lead screens) and the result is an extra photographic effect on the silver halide emulsion layers.

When using intensifying screens in combination with said film a close contact between the film and the screens is essential in order to obtain sharp images, and for this reason intensifying screens are preferably used inside of a film cassette, or an evacuated resin bag.

The fluorescent intensifying screens consist of a thin, flexible base coated with a fluorescent layer containing fluorescent microcrystals, e.g., of calcium tungstate.

Lead intensifying screens are made up from a thin sheet of lead foil preferably stuck onto a thin base such as a sheet of paper or card. Normally two lead screens are used. Lead screens are generally used to bring about an improvement in detail rendering and to cut down the exposure time.

In order to demonstrate quantitatively the increase in visual retrieval of information obtained according to the present invention the term "discernability" has to be explained.

When using black-and-white photosensitive materials, the discernability of relatively large low-contrast details by the radiographer is dependent mainly on the density differences produced in the image, and on the mean density level at which the details are located. At each mean density level a minimum discernable (perceptible) density difference ΔD_{min} can be found (ref. Hitoshi Kanamori, "Determination of Optimum Film Density Range for Röntgenograms from Visual Effects," Acta Radiologica Diagnosic, vol. 4 (1966), pp. 463–476). The determination of said difference depends on the viewing conditions.

The "discernability" (π) corresponds mathematically to 60 the quotient:

$$\frac{\gamma}{D_{\min}}$$

gamma (γ) being expressed as:

$$\frac{dD}{d\log E} = f(\log E)$$

Since

$$\frac{\Delta D}{\Delta D_{\min}}$$

ratio of the maximum densities $(D_1:D_2)$ is the visual 75 represents the amount (ΔN) of just discernable density

differences in a density interval ΔD , π may also be defined as follows:

$$\pi = \frac{\gamma}{\Delta D_{\min}} = \frac{\Delta D}{\Delta D_{\min}} \cdot \frac{1}{\Delta \log E} = \frac{\Delta N}{\Delta \log E}$$

The amount of discernable density-differences and their distribution along the log E-axis (of the sensitometric density (D); versus log exposure (log E) curve) is represented by the so-called "discernability curve."

The area comprised between the discernability curve 10 and the $\log E$ axis is a measure for the discernability content (N) since:

$$\int_{\rm E_0}^{\rm E_{0n}} \frac{\Delta N}{\Delta \log E} \cdot d \log E = N$$

The number "n" of E_0 exposures is sufficiently large to 15 cover the range of exposures in the sensitometric curve.

An experimental way of obtaining the discernability curve will be described now. The number and the distribution along the log E-axis of the just perceptible den-20sity differences recorded by a given radiographic material can be determined experimentally by performing psychometric tests, which consist in subjecting to visual inspection by a large number of observers, under standardised conditions that are representative for radiodiagnostic purposes a series of images made on the radiographic material to be tested, by radiographing a test object, which will now be described in detail.

On the radiographic material, e.g. film material, to be tested are placed stacks of aluminum discs having a di-30 ameter of for example 1 cm. Each disc has a same arbitrary thickness, e.g. 20μ as described in the test of Example 1. Compared with an exposure E₀ received by portions of the film not covered with said discs, the exposure values of the portions under the stacks diminish with a 35value $\sigma \cdot q$, $2\sigma \cdot q$, $3\sigma \cdot q$, . . ., $n\sigma \cdot q$; σ being the radiation absorption coefficient of the disc material (aluminum).

On the basis of the judgement of a large amount of observers, e.g. 10, having normal colour and black-andwhite vision, it can be defined which stack built up by 40 "i" discs is just discernable or perceptible against its background.

At stack "i" the amount of just perceptible density differences ΔN equals 1 and $\Delta \log E = -i\sigma \cdot q$, so that

$$\frac{\Delta N}{\Delta \log E} = k \cdot \frac{1}{i}$$

By repeating the measurement for different E_0 values distributed over the whole sensitometric $(D/\log E)$ curve and plotting

$$\frac{1}{i}$$

against $\log E$ an experimental discernability curve is obtained psychometrically. The area below this curve corresponds with the discernability content (N).

FIG. 1 represents discernability curves of a black-andwhite and colour material the sensitivity of which is practically the same. FIGS. 2 and 3 represent discernability curves explained in Example 1. FIG. 4 represents an absorption curve of a dye image prepared for the purpose 60 of the present invention. FIGS. 5-7 represent transmission curves of filters.

The psychometrical method offers the possibility to determine in a fairly accurate way the visual retrieval of information content in different colour and black-and- 65 white images and to compare them under that aspect. In the examples a more detailed description of said comparative tests is given.

The radiation-sensitive materials for use according to the present invention may contain in addition to the de-70 sired colour coupler, all kinds of ingredients characteristic for silver halide materials used for direct or indirect recording of penetrating radiation.

So, the radiation-sensitive silver halide emulsions may contain sensitizing and/or screening dyes,

According to a special embodiment, selectively working desensitizing dyes are used which lower the sensitivity to visible light without substantially affecting the X-ray sensitivity. For such dyes reference is made to the French patent specification 1,529,155, filed June 21, 1967 by Gevaert-Agfa N.V.

For the purpose of accelerating the development, the exposed silver halide is preferably developed in the presence of water-soluble alkylene oxide condensation products or polymers as described e.g., in the U.S. patent specifications 1,970,578 of C. Schöller and M. Wittwer, Apr. 29, 1941, 2,423,549 of Ferdinand Schulze, issued Apr. 29, 1941, 2,423,549 of Ferdinand Schulze, issued July 8, 1947, 2,441,389 of R. K. Blake, issued May 11, 1948, 2,531,832 of W. A. Stanton, issued Nov. 28, 1950, 2,533,990 of R. K. Blake, issued Dec. 12, 1950 and the United Kingdom patents specifications 991,608 filed June 14, 1961 by Kodak Ltd., 920,637 filed May 7, 1959, 945,340 filed Oct. 23, 1961, 940,051, filed Nov. 1, 1961 and 1,015,023, filed Dec. 24, 1962 all by Gevaert Photo-Producten N.V. For suitable development accelerating polymeric products of another type, reference is made to our published Dutch patent applications 6614230, filed Oct. 10, 1966 and 6614291, filed Oct. 11, 1966. Other compounds which sensitive the photographic emulsion by development acceleration are organic onium compounds and polyonium compounds, preferably of the ammonium or sulphonium type, e.g. quaternary tetraalkylammonium salts, alkyl-pyridinium salts, bis-alkylenepyridinium salts, alkyl-quinolinium salts, and trialkyl sulphonium salts.

The silver halide can further be combined with chemical sensitizers known in the art such as sulphur-containing sensitizing compounds e.g. allyl isothiocyanate, allyl thiourea, reducing compounds such as the tin compounds described in the Belgian patent specifications 493,464, filed Jan. 24, 1950 and 568,687, filed June 18, 1958 both by Gevaert Photo-Producten N.V., or noble metal compounds such as gold, platinum, palladium, iridium, ruthenium and rhodium compounds.

The silver halide emulsions used according to the present invention can also contain known stabilizing agents for silver halide emulsions, e.g. mercury compounds, sulphur compounds such as 1-phenyl-2-tetrazoline-5-thione, 45 the compounds described in the Belgian patent specifications 571,916 and 571,917 both filed Oct. 10, 1958 by Gevaert Photo-Producten N.V., either or not in combination with chemically sensitizing and stabilizing cadmium salts in the light-sensitive material as well as in the developer.

Together with the above-mentioned ingredients, derivatives of tetra-azaindenes, e.g. having the following general formula, can be used as fog-inhibiting compounds in the light-sensitive material:



wherein:

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each of R_1 and R_2 represents a hydrogen atom, an alkyl, an aralkyl, or an aryl group, and

 R_3 represents a hydrogen atom, an alkyl, a carboxy, or an alkoxycarbonyl group.

The X-ray film according to the present invention is not the same as ordinary colour film since it contains a relatively higher amount of silver halide and according to a preferred embodiment a colour coupler that produces a dye having a substantial absorption in two primary colours, e.g. red and green.

For improving the contrast (legibility) between the 75 exposed parts and non-exposed parts, use can be made Б

of a photographic material containing coloured colour couplers or substances e.g. hydrazones which contain the structural group

that form a dyestuff in the bleaching bath by the oxidative copulation with residual colourless colour coupler(s) ¹⁰ which results in a dye image having a gradation opposite to that of the silver image and of the monochromic dye image formed in the exposed parts. The colours of the images having an opposite gradation are different i.e. differ in colour tone. Techniques for producing dye images with opposite gradation and ingredients for that purpose are described in the U.S. patent specifications 3,245,787 of Jozef Frans Willems and Jan Jaeken, issued Apr. 12, 1966, 3,245,788 of Jan Jaeken and Robert Leopold Jansseune, issued Apr. 12, 1966 and 3,310,402 of Jan Jaeken and Hugo Vital Van Goethem, issued Mar. 21, 1967.

The processing of the radiation-sensitive film used for producing colour radiographs according to the present 25 invention may occur in conventional developing apparatus for X-ray film development. The development need not to be followed with a bleaching step for removing the silver image so that a processing as simple as that for producing conventional negative black-and-white radiographs can be applied.

A processing including development, fixation and rinsing, may occur in conventional deep-tank processors including a drier, e.g. the Gevamatic S (trade name) automatic processor for industrial X-ray films, the wet-treatment stations being provided with the appropriate liquid compositions, or in an apparatus wherein the application of one or several of the processing liquids to the exposed material occurs by a lick-roller, a kiss-roller, or any other system capable of applying to one side of the exposed 40 material only a limited and premetered quantum of processing composition. The processing may also be carried out manually by the operator, who attaches the film to clips of a frame, which is successively dipped into the different processing tanks.

Fast processing (development) of the silver halide materials according to the present invention may proceed e.g. as follows: the exposed material is treated at higher temperatures (35 to 45° C.) with an alkaline developing solution containing N-ethyl-N-hydroxyethyl-p-phenylenediamine as developing agent till desired image formation, fixed at the same higher temperatures rinsed and subsequently dried. The whole procedure normally lasts no longer than 3 to 4 minutes. The developing bath preferably contains antifogging agents and/or development ac-55 celerators known to those skilled in the art.

The improved visual retrieval of information from a radiograph produced according to the present invention is based on the fact that the colour image still contains density differences (brightness differences) that are dis- 60 cernable with white light in the high density portions of the image, whereas in a corresponding black-and-white image such differences can no longer be observed. Indeed, a density of 2 in black-and-white photographs means that only a one hundredth part of the total amount of light 65 projected onto said image is transmitted (use of a transparency) or reflected (use of an opaque background). In other words 99% of the incident light is absorbed. In a monochromic colour reproduction, however, a spectral density of 2 means that 99% of the light having a colour 70 complementary to the colour of the light transmitted by the monochromic image is absorbed, but also that the said light of complementary colour still constitutes an amount of light (luminance) transmitted or reflected by the radiograph image.

In a blue image a density of 2, e.g., means that 99% of green and red are absorbed, but that the blue light itself is transmitted or reflected without substantial loss of intensity. Psychometrical tests have revealed that the human eye is particularly sensitive for the perception of brightness differences in the higher density values of a blue image, but we do not exclude other "two third spectrum colours" i.e. colours corresponding with a main absorption in at least two primary colour regions of the visible spectrum, from the scope of the present invention, e.g. absorption of blue and red light.

It is interesting to apply the radiograph materials capable of producing such two third spectrum colour images in the radiography of objects having a certain thickness and complexity e.g. for medical purposes in the radiography of the skull, thorax and abdomen. The increase in retrieved information content by white light inspection of said colour images is higher than for black-and-white images. In other words in the parts of a radiographic negative image corresponding with the soft or easily radiation-penetrable parts of the radiographed object or body part more brightness differences can be visually retrieved with white light. (See FIG. 1.) In FIG. 1 curve A represents the discernability curve of a black-and-white material having a sensitivity that is practically the same as the sensitivity of the colour material. Curve B represents the discernability curve of the colour material inspected with white light.

A further advantage of the present invention resides in the possbility to obtain more information from the lower density portions of the colour image by inspecting it with light, the spectral composition of which is such that it is modulated by the dye image, than by inspecting it with white light. For instance, when a blue image has been produced more information can be retrieved with red light. Indeed, by the inspection with red light a higher image contrast is obtained in the lower density portions (shadow parts of a negative and high lights of a positive).(See FIG. 1, curve C.)

The increase of retrieved information in the lower density portions by coloured light inspection is particularly useful in medical X-ray since now more information can be obtained from the highly radiation-absorbing parts of a body, e.g., the bones.

It is self-explanatary, that, if necessary or desired, positive colour images can be produced instead of negative colour images, e.g. according to a photographic colour reversal process, which includes the following steps; image-wise radiographically exposing a silver halide recording material, developing the exposed silver halide in a black-andwhite developing composition, rinsing, re-exposing the recording material uniformly in order to produce a latent image corresponding with the initially non-irradiated silver halide, developing said latent image in a colour developing composition, bleaching the silver, rinsing and drying the material.

The second exposure can be omitted if the material is treated in a solution of a fogging agent such as hydrazine or a semi-carbazide, e.g. 10 g. of semi-carbazide hydrochloride per litre. The fogging agent may be added directly to the second developer.

Positive colour images can also be produced by means of a process based on the image-wise diffusion of complexed silver halide that is developed with a colour developing agent coupling in oxidized state with a colour coupler or based on the image-wise diffusion of (a) coloured developing agent(s).

The following examples illustrate the present invention, without, however, limiting it thereto.

EXAMPLE 1

(a) Characteristics of the radiograph colour material

A polyethylene terephthalate support subbed on both sides was coated at both sides with a silver bromide/ 75 iodide emulsion (9 mole percent of iodide). The rate of coating was such that per sq. m. the following ingredients were applied:

an amount of silver halide corresponding with 4.25 g. of silver nitrate.

5.5 g. of gelatin.

1.5 g. of a phenol coupler having the following structural formula:



(b) Characteristics of the radiographic black-and-white material

This material was a radiographic black-and-white material suited for radiographic exposure with the aid of 20 tungstate screens and contained at both sides of a subbed polyester resin support a highly sensitive gelatino silver bromide-iodide (3 moles percent of iodide) emulsion coating having a ratio of gelatin to silver nitrate of 1.6, and an amount of silver halide per sq.m. equivalent to 8 g. of 25 silver nitrate.

(c) Exposure, processing and determination of the discernability curves of the colour and black-and-white materials

On sheets of the radiographic materials described 30 under (a) and (b) stacks of aluminum discs were placed. Each disc had a thickness (q) of 20μ and stacks contained from 1 to 54 discs.

Both materials were exposed with an X-ray tube (tungsten anti-cathode) working at 60 kv.

35A series of exposures of increasing value was made on pairs of sheets of said colour and said black-and-white material to be compared. The exposure (the different log E_0 values) embraced the whole sensitometric curve, and were obtained by step-wise increasing the ma. input of 40 the cathode, the exposure time and/or decreasing the distance of the exposure source from the radiation-sensitive sheets.

In Table 1 hereinafter these exposure conditions are set forth. The exposure given to each pair of sheets consisting of a black-and-white material sheet and a colour 45 material sheet in the portions not covered with the stacks of aluminium discs was called E₀.

50					1 sec. at-	т, 0.0				-
	ma.	400 1	ma.	400	ma.	80	5 ma. 20 ma.		5 ma.	
	LogE	d in cm.	Log E	d in cm.	Log E	d in cm.	Log E	d in cm.	Log E	d in cm.
55	2.80 3.10	119 84	$1.90 \\ 2.20$	168 119	1.20 1.50	168 119	0.60 0.75	168 141	0.00 0.15	168 141
	3.40	53 	2,35 2,50 2,65		$\begin{array}{c} 1.65 \\ 1.80 \end{array}$	100 84	0.90 1.05	119 100	0.30 0.45	119 100

NOTE.-d=distance; T=exposure time.

Operating that way, the least and the most exposed 60 test sheets received an exposure (E_0) corresponding with 0.05 ma. and 16 ma., respectively.

Thus, it was possible to compare the discernability of the black-and-white material and colour material for the whole sensitometric curve.

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On the basis of the judgement of 10 observers with normal black-and-white and colour vision the number of discs forming a particular stack corresponding with a print that was just discernable against the background done for each pair of strips that had received the same 70 exposure.

Compared with an exposure E₀ received by portions of the film sheets not covered with said stacks of increasing amounts of aluminum discs, the exposure values of the portions of the radiographic material under the 75 lasted 3 min. 30 sec. (rapid processing).

stacks diminish with a value $\sigma.q$; $2\sigma.q$; $3\sigma.q$; . . . $n\sigma.q$ (σ is the radiation absorption coefficient of the aluminium).

From the said judgement for each strip a stack print "i" with an amount of "i" discs is statistically found to be just discernable against the background exposure (E_0) involved.

Having determined the just discernable print of stack "i" for each applied E_0 exposure, we may define the just 10 discernable density difference ΔN as being equal to 1 (ΔN =1). The "discernability" $\Delta N/\Delta \log E$ is directly proportional to 1/*i* since $\Delta \log E$ = $-i.\sigma.q$.

Effecting the said statistical measurement for all the exposures E_0 , the conditions of which are listed in Table 15 curve is obtained. In other words by plotting 1/i against the applied long E_0 values we obtain a discernability curve for the colour and for the black-and-white material.

The discernability of the colour material is a function of the colour of the light used for the visual inspection. The surface below the discernability curve is a measure for the discernability content (N) or total retrievability of information by the human eye from the recording material tested.

In FIG. 2 and 3 curve A represents the discernability curve of the black-and-white material b) inspected with white light.

Curve B in FIG. 2 represents the discernability curve of the colour material a) inspected with white light.

Curve C in FIG. 2 represents the discernability curve of the colour material a) inspected with red light (the transmission curve of the applied red light filter) is given in FIG. 5.

In FIG. 3 curve D repersents the total discernability curve of the combination of the inspection with white light and red light of the colour material a).

In the following Table 2 the surface below said experimental discernability curves is set forth, the area comprised between the black-and-white discernability curve (curve A in FIG. 2 and FIG. 3) and the log E axis arbitrarily given the value 100 and the area comprised below the other curves being calculated on a procentual basis thereon.

1110000					
Surface	Δ in percent				
100 .					
132.5	+32.5				
81	-19				
140	+40				
	Surface 100 - 132.5 81 140				

TABLE 2

From the said curves can be learned that the discernability content under white light viewing conditions is markedly improved in the higher density values of the monochromic colour material as compared to that of the black-and-white material, and that the discernability under red light viewing conditions (light absorbed by the monochromic dye image) is improved in the lower density range (visual increase of contrast in the lower density portions) when compared with the white light inspection.

The absorption curve of the dye image is represented in FIG. 4.

The colour material was developed with a developer having the following composition:

	G.
N-hydroxyethyl-N-ethyl-p-phenylenediamine	8
Hydroxylamine	1.5
Sodium sulphite (anhydrous)	4
Potassium bromide	1
Potassium carbonate (anhydrous)	65
Water till 1000 ml.	
(pH about 10.8).	

The development was carried out at 41° C. The whole procedure of development, fixing, rinsing and drying

	Th	e black-an	d-white	mat	erial	was (developed	at 40°	с.
in	a	developer	having	the	follc	wing	composit	ion:	

Water $(40^{\circ} C_{\rm o}) 800 {\rm m}$	в.	
Metol (trade name)	4	-
Anhydrous sodium sulphite	65	Э
Hydroquinone	10	
Anhydrous sodium carbonate	45	
Potassium bromide	5	
Water till 1000 ml.		10

The whole procedure of development, fixing, rinsing and drying also lasted only 3 min. 30 sec.

Preparation of the phenol coupler

15 (a) 154 g. (1 mole) of 5-nitro-2-aminophenol were dissolved in 1.5 l. of water-free acetone. Under stirring 100 g. (1.2 mole) of anhydrous sodium hydrogen carbonate were added. At 20° C. 109 ml. (1 mole) of 2-furoylchloride were dropwise added. The temperature rose from 20 to 30° C. and the final product started to precipitate. The obtained mixture was stirred for about 4 hours until all the 5-nitro-2-aminophenol was transformed. The precipitate formed was filtered with suction and washed with acetone, until the filtrate was colourless. 25 In order to eliminate any sodium hydrogen carbonate still present, the precipitate was stirred for about 40 min. in 1.5 litre of hot water, filtered with suction and washed with water. The purified precipitate was dried in a cold ventilated drying oven. Yield: 220 g. (89%). Melting 30 point: beyond 260° C.

(b) 327 g. (1.5 mole) of 2-(2'-furoylamino)-5-nitrophenol prepared as described under (a) together with 25 ml. of Raney nickel in 3 litres of dimethylformamide were reduced at 60-65° C. under 1500 p.s.i. of hydrogen pres- 35 sure. The reaction lasted about 3 hours. After filtering off the Raney nickel, the filtrate was concentrated by evaporation on the water jet pump, and allowed to solidify with stirring under water. The precipitate obtained was filtered with suction, washed with water and dried. Yield: 40 262 g. (91%). Melting point: 184-186° C.

(c) 218 g. (1 mole) of 2-(2'-furoylamino)-5-aminophenol prepared as described under (b) and 386 g. (1.2 mole) of hexadecenylsuccinic anhydride were refluxed for 30 min. in 3 litres of acetonitrile. In order to avoid crystallization from the reaction mixture, 60 ml. of acetic acid ⁴⁵ were added to the acetonitrile. After cooling, the precipitate formed was filtered with suction, dried and recrystallized from dichloroethane. Yield: 442 g. (82%). Melting point: 134° C.

EXAMPLE 2

The same materials (a) and (b) as described in Example 1 were used for the exposure to a skull phantom and thorax phantom.

Both films were used in a film cassette having incorpo- 55 rated therein calcium tungstate screens (intensifying coefficient 2).

For the exposure using the skull phantom as an object an exposure corresponding to 150 ma./60 kv. was applied. The distance between the film and the X-ray radiation 60 source was 100 cm.

For the exposure using the thorax phantom as object an exposure corresponding to 15 ma./75 kv. was applied. The distance between the film and the X-ray 65 radiation source was 180 cm.

The development was the same as that described in Example 1.

More information was visually retrieved by white light inspection of the high density parts of both the skull phan- 70 tom and thorax phantom monochromic colour images than in the corresponding image built up in the blackand-white material by a silver image alone.

A higher information content was retrieved from the monochromic colour images in the lower density por- 75 melting point: 159° C. (see for the preparation U.S. patent

tions by inspection with red light. This was due to an observed increase in contrast in said portions.

The gradation of the silver image in the black-and-white material was 2.7, and the maximum density was 3. The maximum density of the colour image measured through red filter (transmission spectrum in FIG. 5) amounted to 4.5. The maximum density of the colour image measured through green filter (transmission spectrum in FIG. 6) was 3.8. The maximum density of the colour image measured through blue filter (transmission spectrum in FIG. 7) amounted to 2.2.

The gradation of the straight line curve part of a simultaneously printed wedge image measured through the red filter was 3.77.

The gradation of the colour image measured through the green and blue filter amounted to 2.66 and 1.50 respectively.

Variations in silver halide content, colour coupler content and gelatin content resulted in the following sensitometric properties listed in Table 3.

TABLE 3

No. of the colour material	Silver halide expressed as silver nitrate (g./sq. m.)	Colour coupler (g./sq. m.)	Gelatin (g./sq. m.)	Grada- tion	Relative speed in respect to the black- and-white material (log values)
1	. 8	3	11.2	3.05	-0.09
3	12	3	11.2	2.98	0.12
4	10	2.25	8.4	2.17	-0.17 -0.11
5	Ğ	3.75	8.4	1.67	-0.10
6	6	3.75	14	2.22	-0.23
7	10	2.25	10	2.57	-0.16
8	10	3.75	10	3.10	+0.06
9	10	3.75	14	2.42	-0.12
Black-and-white emulsion	16		10	2.80	

The gradations of the images obtained with the colour materials were measured through red filter (transmission curve FIG. 5).

The gradation of the image of the black-and-white material was measured with the white light.

A decrease with 0.30 of the speed in respect of the black-and-white material means that the speed is 2 times as small. An increase of 0.30 of the speed in respect of that of the black-and-white material means that the speed was doubled.

Speed values were measured at a density 1 above fog. For the colour materials the density was measured through the already mentioned red filter.

The Callier factor of colour material No. 1 at wave-50 lengths 450 nm. and 640 nm. (minimum and maximum absorption) amounted to 1.45 and 1.10 respectively. The black-and-white material at same wavelengths yielded the quotients 1.57 and 1.47 respectively, which proves the higher light-scattering power of the silver image of the black-and-white material than of the silver image and colour image contained in the developed but non-bleached colour material.

EXAMPLE 3

Example 2 is repeated with the proviso, however, that the photographic material in addition to the phenol coupler used therein contains a 100 mg. per sq. m. of a pyrazolone coupler having the following structural formula:



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specification 3,325,482 of Marcel Jacob Monbaliu, Arthur Henri de Cat and Raphael Karel van Poucke, issued June 13, 1967).

Another suitable mixture of colour couplers for use according to the present invention consists of:



melting point: 96° C. (see for the preparation British patent specification 519,208, filed Sept. 17, 1938 by J. 15 Desire Kendall and R. B. Collins, p. 3), and



Melting point: 729° C. (see for the preparation J.A.C.S.: 25 73 (March 1951), 919-926).

I claim:

1 A process for recording for visual retrieval information obtained by means of ionizing radiation including X-rays, alpha, beta or gamma rays and neutron radiation 30 or secondary radiation derived from said ionizing radiation including electrons, ultraviolet light or visible light, said process comprising the steps of:

(1) information-wise modulating said radiation and exposing to the radiation thus obtained the emulsion 35 layers of a photographic silver halide material comprising a colorless transparent support and at least one silver halide emulsion layer, each such layer containing a color coupler capable of producing on color developing with a p-phenylene diamine developing 40 agent an image of a quinonimine dye having its main spectral absorption in the region of 700-600 nm.; an absorption in the region of 600-500 nm. at least 30% as great as but less than its absorption in the region of 700-600 nm., and in the region of 400-500 nm. 45 at 450 nm. an absorption less than the absorption in the region of 600-500 nm., with its maximum absorption being in the region of 570-660 nm., said silver halide material having in the emulsion layers thereof an aggregate amount of silver halide corresponding to about 5-16 g. of silver nitrate per sq. m.,

- (2) developing said latent silver image in each layer with an aromatic primary amino photographic developing agent reacting with said color coupler to form said quinonimine dye image together with a 55 silver image, and
- (3) visually retrieving the information thus recorded in the form of a mixture of said silver and said dye images by inspection with white or red light.

2. A process according to claim 1 wherein the color $_{60}$ coupler corresponds to the following general formula:



3. A process according to claim 2 wherein at least one of the R groups represents a 2-furoyl group, a 2-thienoyl group, an aliphatic carboxylic acyl group, an aliphatic sulphonic acyl group, an aliphatic sulphonic acyl group, 75 group, an aliphatic carboxlic acyl group, an aliphatic

an aromatic carboxylic acyl group or an aromatic sulphonic acyl group.

4. Ahe process according to claim 1 wherein said pphenylene diamine color developing agent is used selected from the group of p-phenylene diamine, N,N-diethyl-pphenylene diamine, N-butyl, N-sulphobutyl-p-phenylene diamine, 2-amino-5-diethylamino toluene hydrochloride and 4-amino-N-ethyl, N-(β -methane sulphonamidoethyl) m-toluidinesesquisulphate monohydrate and N-hydroxyethyl, N-ethyl p-phenylenediamine.

5. A process according to claim 1 wherein the ratio of the maximum spectral density at the absorption maximum of the dye image to the maximum spectral density at the absorption maximum of the dye image to the maximum spectral density of the silver image in the visual spectral range is about 1:1 to 5:1 when viewed under white light.

6. A process according to claim 1 wherein the photographic silver halide material contains an amount of silver halide equivalent to 5 to 16 g. of silver nitrate per sq. m.

7. A process according to claim 1 wherein the photographic material includes a transparent resin support having on each of its sides a silver halide emulsion layer of the described composition.

8. A process according to claim 1 wherein the photographic material contains at least one silver bromoiodide emulsion layer.

9. A process according to claim 8 wherein said silver halide emulsion layer contains a silver bromoiodide containing up to 10 mole percent of iodide.

10. A process according to claim 9 wherein the silver bromoiodide contains from 10 to 2 mole percent of iodide.

11. A process according to claim 3 wherein the color coupler has the following structural formula:



12. A photographic material which comprises a colorless support and at least one silver halide emulsion layer, each such emulsion layer containing at least one color coupler producing on color development with a p-phenylene diamine developing agent a quinonimine dye image that absorbs in the region of 700-600 nm. and in the region of 600-500 nm. to the extent of at least 30% of its absorption in the region of 700-600 nm. and has in the region of 400-500 nm, at 450 nm. a spectral absorption not higher than the maximum of the absorption being situated in the region of 600-500 nm., the aggregate amount of silver halide in the material corresponding to 5 to 16 g. of silver nitrate per sq.m.

13. A photographic material according to claim 12 wherein said material contains a plurality of said silver halide emulsion layers and each such layer contains at least one color coupler which is the same in all such layers and yields dye images of the same color.

14. A photographic material according to claim 12 wherein each such emulsion layer contains a color coupler according to the following general formula:



acyl group.

15. A photographic material according to claim 14 wherein at least one of the R groups represents a 2furoyl group, a 2-thienoyl group, a sulphonyl thienyl sulphonic acyl group, an armoatic carboxylic acyl group or an aromatic sulphonic acyl group.

16. A photographic material according to claim 12, which material comprises at least one silver halide emulsion layer which contains said color coupler and silver halide in an excess of 50 to 150% in respect to the equivalent ratio necessary in the dye forming reaction.

17. A photographic material according to claim 12 wherein the said material has a transparent support and on each side of the support one of said silver halide 10 emulsion layers.

18. A photographic material according to claim 15 wherein the color coupler corresponds to the following structural formula:



с́н₂соон

19. A process for recording for visual retrieval information obtained by means of ionizing radiation including X-rays, alpha, Beta or gamma rays and neutron radiation or secondary radiation derived from said ionizing radiation including electrons, ultraviolet light or visible light, said process comprising the steps of:

- (1) information-wise modulating said radiation and exposing to the radiation thus obtained the emul-30 sion layers of a photographic silver halide material comprising a colorless transparent support and at least one silver halide emulsion layer, each such layer containing a mixture of a first color coupler capable of producing on color development with a 35 p-penylene diamine developing agent an image of a quinonimine dye and a second color coupler capable of forming on color development with said pphenylene diamine developing agent an image of an azomethine dye, the composite image of said dyes 40 having its main spectral absorption in the region of 700-600 nm., an absorption in the region of 600-500 nm. at least 30% as great as but less than its absorption in the region of 700-600 nm. and in the region of 400-500 nm. at 450 nm. an absorption less 45 than the absorption in the region of 600-500 nm., with its maximum absorption being in the region of 570-660 nm., said silver halide material having in the emulsion layers thereof an aggregate amount of silver halide corresponding to about 5-16 g. of silver 50 nitrate per sq. m.
- (2) developing said latent silver image in each layer with an aromatic primary amino photographic de-

veloping agent reacting with said color coupler to form said quinonimine dye image together with a silver image, and

(3) visually retrieving the information thus recorded in the form of a mixture of said silver and said dye images by inspection with white or red light.

20. A process according to claim 19 wherein the color coupler forming the quinonimine dye is a phenol type or naphthol type coupler and the color coupler forming the azomethine dye is a pyrazolone type coupler.

21. A photographic material which comprises a colorless support and at least one silver halide emulsion layer each such layer containing a mixture of a first color coupler capable of producing on color development with a

p-phenylene diamine developing agent an image of a quinonimine dye and a second color coupler capable of forming on color development with said p-phenylene diamine developing agent an image of an azomethine dye, the composite image of said dyes having its main spectral absorption in the region of 700-600 nm., an absorption in the region of 600-500 nm. at least 30% as great as but less than its absorption in the region of 700-600 nm. at 450 nm. an absorption less than the absorption in the region of 600-500 nm. at 450 nm. an absorption less than the absorption in the region of 600-500 nm. at 450 nm. an absorption less than the absorption being in the region of 600-500 nm., with its maximum absorption being in the region of 570-660 nm., said silver halide material having in the emulsion layers thereof an aggregate amount of silver halide corresponding to about 5-16 g. of silver nitrate per sq.m.

22. The photographic material of claim 2 wherein said first color coupler is a phenol or naphthol type color coupler for cyan and said second color coupler is a pyrazolone or indazolone type color coupler for magenta.

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