

[54] **NEUTRON DETECTION AND RADIOGRAPHY**  
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[52] U.S. Cl. .... **250/391; 250/483**  
 [51] Int. Cl. .... **G01t 3/00**  
 [58] Field of Search .... 250/312 VT, 483, 486, 390, 250/391, 392

[56] **References Cited**  
**UNITED STATES PATENTS**  
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3,140,397 7/1964 Henry ..... 250/472  
 3,617,285 11/1971 Staudenmayer ..... 250/483 X  
 3,617,743 11/1971 Rabatin et al. .... 250/483 X  
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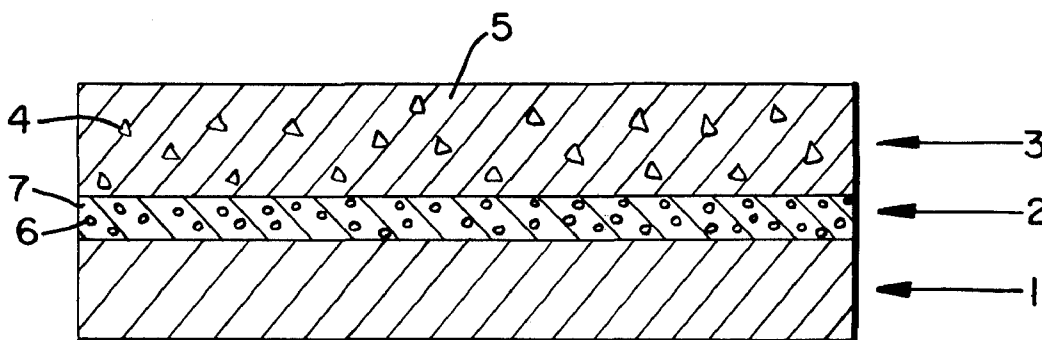
**OTHER PUBLICATIONS**

Radiation Shielding, by Price et al., Pergamon Press 1957, pp. 333, 334, 335.

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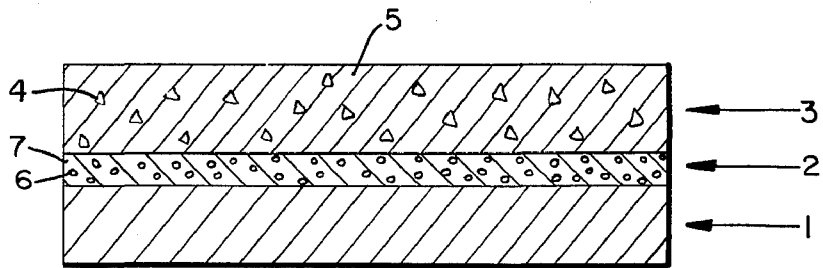
[57] **ABSTRACT**  
 An improved method of recording neutron images which comprises imagewise irradiating with neutrons an intensifying screen containing a gadolinium compound that fluoresces when struck by x-rays and subjecting the fluorescent light pattern resulting from the impact of the neutrons on the screen onto a photographic material.

**29 Claims, 1 Drawing Figure**



PATENTED JUN 24 1975

3,891,852



## NEUTRON DETECTION AND RADIOGRAPHY

This invention relates to the detection of neutrons and the recording of neutron images and to the use of particular substances, materials and devices in said detection and recording.

The interest in neutron recording and detection includes among others neutron dosimetry, neutron diffraction, neutron radiography and neutron image conversion in a visible image e.g., in an image intensifier tube. Neutron radiography is a well known valuable complement to X-ray and gamma ray radiography.

As is known e.g., from H. Kallmann, Research 1, (1948) Nr. 6, pages 254-260, neutrons do not substantially affect a photosensitive silver halide directly. Therefore in common neutron radiography a combination of silver halide film with a neutron sensitive intensifying screen is applied.

In general, neutron radiation-sensitive screens can be divided into three classes according to the function they have to perform.

The first class includes screens which are called here "neutron conversion screens." Such screens have the property to produce ultraviolet light or visible light photons in a fluorescent screen contacting a photocathode that emits photoelectrons under the influence of the fluorescent light. Such screens may find application in image intensifier or image conversion tubes similar to those known from X-ray radiography (ref. G.J. Van der Plaats, Medical X-ray Technique (1959) — Phillips' Technical Library, pages 103-108). In such tubes the photo-electrons emitted by the photocathode are accelerated electrically in vacuum and an electric or magnetic focusing field is used to focus the electron image on another fluorescent screen which is sensitive for fast moving electrons. The photo-electrons are thus transformed into visible light in a way similar to that known from television picture tubes.

The second class includes screens which are called here "fluorescopic screens." Such screens have the function of producing a directly viewable image in correspondence with the neutron image. The screen is viewed e.g., by means of optical means or photographed for the purposes of cineradiography or for producing television pictures. The fluorescopic image may be intensified with an electronic image intensifying tube before being viewed or photographed.

The third class includes screens which are called here "intensifying screens." Such screens have the function to transform the neutron radiation into electromagnetic radiation or high energy particle radiation e.g.,  $\beta$  or  $\alpha$ -rays, for which a photographic material directly contacting the screen is sensitive.

Normally the intensifying screens are used in combination with silver halide emulsion film sheets that together and in immediate contact with the screen(s) are mounted in a light-tight cassette.

There are two film-exposure techniques. In one, the "direct-exposure method," the photographic film and the screen in which the neutron energy is converted or transformed in energy for which the photographic film is sensitive are exposed together to the neutron beam to be detected or recorded, whereas in the other method, the "transfer method," only a screen is exposed to the neutron beam; by the neutron bombardment the screen obtains a radioactive pattern corresponding with the neutron beam pattern. This radioac-

tive film is placed next to the photographic film. The film is then exposed by the decay radiation from the screen. (ref. Nucleonics, 20 (September 1962) No. 9, page 77).

There are three basic types of intensifying screens used in thermal neutron radiography, viz. granular, glass and metal foil screens. M. R. Hawkesworth et al. in the Journal of Scientific Instruments 3 (November 1970) Nr. 11, pages 851-854, describes as granular intensifying screen a screen containing a 1:2:1 (by weight) mixture of lithium-6 fluoride, zinc sulphide and perspex having a thickness of 0.65 mm, as metal screen a 25  $\mu\text{m}$  foil of gadolinium and as glass screen a sheet of lithium-6 oxide loaded, cerium activated, scintillator glass 1.3 mm in thickness.

The metal foil screens have to be divided in two types viz. metal screens for direct exposure and metal screens for transfer exposure.

The most useful metal screen for direct exposure is the gadolinium metal screen, which has a very high thermal neutron absorption coupled with the immediate emission of  $\beta$ -particles of low energy (70 keV). The screen has therefore extremely-high resolving power. However, the 70 keV electrons carry only 1/68 of the energy of the  ${}^6\text{Li}(n,\alpha){}^3\text{T}$  taking place in the above mentioned granular lithium-6 fluoride-zinc sulphide screen. The basic reaction in such a screen is  ${}^6_3\text{Li} + n \rightarrow {}^3_1\text{T} + \alpha + 4.79 \text{ MeV}$ . Taking into account the rather low activity of the gadolinium metal screens the fastest silver halide films have to be used in conjunction therewith. The gadolinium metal screens are insufficiently selective to detect neutrons in the presence of  $\gamma$ -rays. Therefore the metal foil screens in order to give perfect discrimination against  $\gamma$ -rays are used in the transfer technique. Other ways to exclude  $\gamma$ -radiation outside of the nuclear reactor are described in The Journal of Photographic Science, Vol. 19, 1971, page 108.

Most metals, unlike gadolinium, emit  $\beta$ -particles some time after neutron absorption. If such a foil is exposed behind an object in a neutron beam the neutron radiographic image will be stored in the foil, which can be removed from the beam after exposure and pressed against a suitable photographic film. The radiograph will then be produced as the foil activity decays. The metals most often used for this work are dysprosium and indium. The transfer technique takes more time than the direct exposure technique.

It is an object of the present invention to provide a neutron detection and recording technique of improved speed.

It is another object of the present invention to use in neutron detection and neutron radiography a combination of photographic materials and fluorescent substances that is particularly useful for that type of detection and recording.

Other objects and advantages of the present invention will become apparent from the further description and example.

It has now been found that gadolinium compounds that have the property of fluorescing when struck with X-rays have a very effective neutron stopping power and have the property of very effectively transforming captured neutron radiation into visible or near visible radiation for which silver halide is inherently sensitive or can be made sensitive by spectral sensitization.

Said gadolinium compounds as can be learned from comparative tests have a much larger "relative intensi-

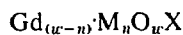
fication factor" than pure gadolinium metal intensifying screens.

By "relative intensification factor" is to be understood here, a factor measured at a pre-elected density  $D$ , indicating the dosis (neutrons per  $\text{cm}^2$ ) required to produce this density when a silver halide film is exposed to neutrons with a "standard screen" divided by the dosis required to produce the same density with the screen to be tested. Exposure conditions, film and developing conditions are kept constant for the comparative tests.

In accordance with the present invention it has been discovered that gadolinium compounds of the oxide, oxyhalide, and oxysulphide type are particularly valuable substances for the detection and recording of neutron beams. Preferred substances for the purpose of the invention contain gadolinium as "host" metal in a phosphor in which (an) other rare earth metal(s) is (are) present as "fluorescence activating metal."

Visible light emitting neutron detecting screens applied according to the present invention are preferably gadolinium oxysulphide or oxyhalide fluorescing substances activated with at least one other selected rare earth metal e.g., terbium, dysprosium, erbium, europium, holmium, neodymium, praseodymium, samarium, thullium or ytterbium.

Particularly suited phosphors for use in neutron radiography correspond to the following general formula:



wherein:

$M$  is at least one of the metals terbium, dysprosium, erbium, europium, holmium, neodymium, praseodymium, samarium, thullium or ytterbium,

$X$  is sulphur or halogen e.g., chlorine, bromine or fluorine,

$n$  is 0.0002 to 0.2, and

$w$  is 1 when  $X$  is halogen or is 2 when  $X$  is sulphur.

The preparation of Rare Earth Oxyhalides and Oxide Luminescent Materials has been described, e.g., by J. G. Rabatin in U.S. Pat. No. 3,607,770 and in the French Pat. No. 2,021,398.

Gadolinium oxyhalides activated with dysprosium are more particularly described in the United States Patent Application Ser. No. 769,922, gadolinium oxyhalides activated with terbium are described in U.S. Pat. No. 3,617,743, gadolinium oxybromide activated with erbium has been described in the U.S. Pat. No. 3,546,128. Fluoro-substituted europium activated gadolinium oxides have been described in the U.S. Pat. No. 3,415,757.

Gadolinium oxysulfide activated with other rare earth elements has been described in the U.S. Pat. No. 3,418,246 and by S. P. Wang et al. IEEE Transactions on Nuclear Science Vol. NS-17 (February 1970) p. 49-56; and by R. A. Buchanan IEEE Transactions on Nuclear Science, February 1972, pages 81-83.

Fluorescent gadolinium compounds that may be used according to the present invention are mentioned in the following documents: the United Kingdom Pat. Nos. 1,018,005 — 1,022,930 — 1,284,296 — 1,131,956 — 1,110,290 — 1,122,923 — 1,128,512 — 1,254,271 — 1,257,322 — 1,266,407 — 1,248,299 — 1,249,544 — 1,279,450 — 1,247,602 — 1,263,038 and 1,269,329, in the U.S. Pat. Nos. 3,415,757 — 3,434,863 — 3,301,791 — 3,282,856 — 3,502,590 — 3,562,174 — 3,563,909 — 3,484,381 — 3,418,246 — 3,418,247 —

3,634,282 — 3,546,128 — 3,574,131 — 3,574,129 and 3,661,791, in the Canadian Pat. Nos. 799,899 and 816,628, in the published German Pat. Nos. 1,284,296 — 1,222,610 — 1,592,884 — 1,915,360 — 1,935,103 — 2,051,262 — 2,051,240 — 2,108,676 and 2,201,271, in the published Dutch Pat. No. 66/3921 and the French Pat. Nos. 1,468,075 — 1,501,441 — 1,504,341 — 1,550,113 — 1,580,544 — 1,542,140 — 2,021,398 and 2,039,921.

Gadolinium compounds that emit in the ultra-violet and/or visible spectrum range are very useful for neutron radiography with silver halide recording materials.

A high speed neutron sensitive intensifying screen contains e.g., terbium-activated gadolinium oxysulphide that has emission peaks at 490 and 540 nm and falls within the scope of the above general formula.

Although in the fluorescent screens for use in neutron radiography according to the present invention preferably only fluorescent compounds are used that contain gadolinium, we do not exclude screens that contain the fluorescent gadolinium compound(s) in admixture with other phosphor substances that fluoresce when struck by X-rays and/or  $\beta$ -rays. Thus, e.g., a suitable fluorescent screen contains a mixture of 25:75 by weight of:

A. yttrium oxysulphide activated with from 0.1 to 10 % by weight of terbium or activated with terbium and dysprosium, and

B. gadolinium oxysulphide activated with terbium or dysprosium is particularly useful for its high visible light emission through neutron exposure.

By spectral sensitization a silver halide recording material can be made optimally sensitive for the visible light e.g., green light emitted by the fluorescent gadolinium compound.

By using a plurality of fluorescent gadolinium compounds in a plurality of different screens or by using a fluorescent screen containing a mixture of different gadolinium fluorescent compounds of the above general formula a fluorescence over the whole visible spectrum can be obtained, so that such combination is particularly useful for recording with silver halide recording elements that have been made spectrally sensitive for light of the whole visible spectrum.

The selected fluorescent gadolinium containing compound(s) is (are) in the form of a layer applied to a support or applied as a self-supporting layer or sheet. Particularly suited fluorescent layers or sheets have a thickness of preferably 10 to 300 microns and contain the fluorescent compound(s) or phosphors e.g., dispersed in a binder or in the form of a vapour deposited or sintered particle layer either or not in the presence of a glassy material.

The binder if any is used, is e.g., an organic high molecular weight polymer. Preferred binding agents are, e.g., cellulose nitrate, ethyl cellulose, cellulose acetate, polyvinyl acetate, polystyrene, polyvinylbutyral, polymethylmethacrylate and the like.

The proportion of high molecular weight polymer binder to fluorescent material is in general within the range of 5-15% by weight. A preferred grain size of the fluorescent gadolinium compounds is in the range of about 1 to 20 microns.

The surface of the fluorescent material layer may be protected against moisture and mechanical damage by a coating of an organic high molecular weight polymer

applied to a thickness of 0.001 to 0.05 mm. Such protecting coating is, e.g., a thin film of cellulose nitrate, cellulose acetate, polymethyl methacrylate and the like.

Besides the fluorescent light impinging normally to the silver halide containing layer there is always an amount of diffuse radiation in the fluorescent screen giving rise to image unsharpness. The image sharpness is improved considerably by incorporating a fluorescent light-absorbing dye called here "screening dye" into the fluorescent screen material e.g., in the fluorescent layer or into an adjacent layer thereto, e.g., a covering layer or subjacent antihalation layer. As the diffused oblique radiation covers a larger path in the screen material it is attenuated by the screening dye to a greater extent than the radiation impinging normally. The term "screening dye" includes here dyestuffs i.e., coloured substances in molecularly divided form as well as pigments.

Diffuse radiation reflecting from the support of the fluorescent screen material is mainly attenuated in an antihalation layer containing the screening dyes subjacent to the fluorescent layer.

The use of screening dyes in a covering layer to the fluorescent layer mainly reduces the strength of the obliquely emitted light originating from the fluorescent layer.

An appropriate screening dye for use in the fluorescent screens emitting in the green part (500-600 nm) of the visible spectrum is, e.g., Neozapon Fire Red (C.I. Solvent Red 119), an azochromium rhodamine complex. Other suitable screening dyes are : C.I. Solvent Red 8, 25, 30, 31, 32, 35, 71, 98, 99, 100, 102, 109, 110, 118, 124 and 130.

The screening dye has not to be removed from the fluorescent screen material and therefor may be any dye or pigment absorbing in the emission spectrum of the fluorescent substance(s). Thus a black substance such as carbon black incorporated in the antihalation layer of the screen material yields quite satisfactory results.

The screening dye(s) is (are) preferably used in the antihalation layer in an amount of at least 0.5 mg per sq.m. Their amount in the anti-halation layer is not limited.

Very good results are obtained with the screening dye(s) in the antihalation layer and in the layer containing the fluorescent substances. In that case the fluorescent layer contains e.g., the screening dye or dyes in an amount of 5 mg per sq.m. The amount of screening dye(s) in the fluorescent layer and/or covering layer may be adapted to the results of image sharpness and intensity of emitted radiation aimed at.

The present invention includes the use of fluorescent gadolinium compound-containing screens in neutron-radiography in conjunction with an other neutron absorbing screen e.g., of the metallic, glassy or granular type. Thus, e.g., the combination with gadolinium, dysprosium, or indium metal screens, the latter two screens being used e.g., in the mentioned "transfer technique." The invention includes likewise the use of fluorescent gadolinium compound-containing screens in neutron radiography in conjunction with metal screens that have a relatively high neutron absorption e.g., an absorption at least as high as lithium in order to remove a certain amount of diffuse neutron rays to improve thereby image-sharpness. An analogous tech-

nique in which an image-sharpness improving metal screen is used in conjunction with a fluorescent screen but for use in X-ray radiography has been described in the United Kingdom Pat. No. 61,050/71 filed Dec. 31, 1971 by Agfa-Gevaert N.V.

Metal screens with a high neutron absorption power may be made of the metals cadmium, gadolinium, europium and samarium or alloys thereof.

Preferred neutron radiographic combinations for use according to the present invention employ in addition to the fluorescent screen a photosensitive element comprising a suitable support bearing photosensitive silver halide. Said silver halide may be present in a layer or coating such as a single coating or a duplitzed or dual coating, i.e., in a material having a silver halide emulsion layer on each side of a support. Suitable supports are those having the properties to permit their ready passage through a rapid automatic processor. The support should therefore be reasonably flexible and preferably transparent but able to maintain the dimensional stability and integrity of the various coatings thereon. Typical film supports are cellulose nitrate, cellulose ester, polyvinyl acetal, polystyrene, polyethylene terephthalate, and the like. Supports such as cards or paper that are coated with  $\alpha$ -olefin polymers, particularly polymers of  $\alpha$ -olefins containing two or more carbon atoms, as exemplified by polyethylene, polypropylene, ethylene-butene copolymers and the like, give good results.

In order to improve image sharpness dyes are used in the silver halide emulsion recording material which dyes are called hereinafter "filtering dyes." They are preferably incorporated in a hydrophilic colloid layer e.g., between the silver halide emulsion layers and/or in the emulsion layers themselves. They may, however, likewise be incorporated in one or more subbing layers or in an antihalation layer at either side of the support and even in the support, e.g., giving it a blue aspect preferably offering it a specular absorption density reaching 0.45 in the 480 to 700 nm wavelength range. The dyes have, however, preferably such chemical and/or physical characteristics that they can be removed or decolorized in one of the processing baths.

According to a preferred embodiment of the present invention a filtering dye or mixture of filtering dyes absorbing in the wavelength range of about 480 to 600 nm is used when fluorescent screens are applied that emit mainly green light (480-600 nm) by neutron exposure.

The amount of filtering dye is preferably in the range of 25 to 1,000 mg per sq.m but here likewise lower or higher amounts may be appropriate according to the result aimed at.

Suitable filtering dyes that can be removed from hydrophilic colloid layers are e.g., those listed in table 1.

Table 1

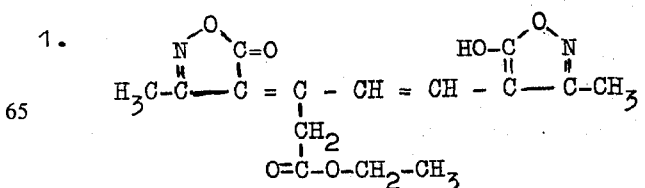
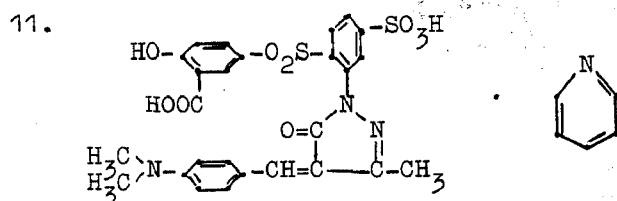
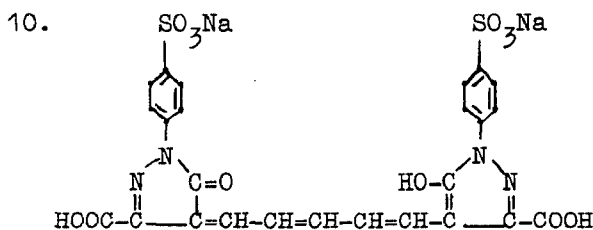
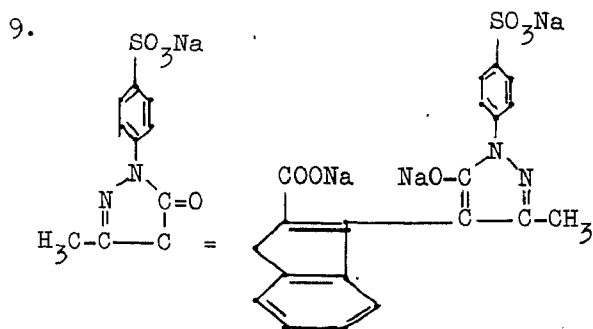
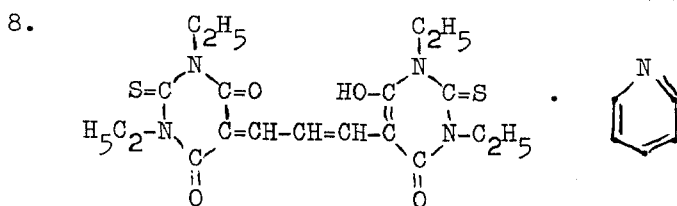




TABLE 1—Continued



## 12. "Filterblaugrün" ® Farbwerke Höchst

In the radiographic combination of neutron-fluorescent screens and silver halide radiographic materials used according to the present invention, the screens may be arranged separately from the light-sensitive silver halide material or they may form with the silver halide emulsion an integral arrangement so that on one and the same support both a silver halide emulsion and a neutron-sensitive fluorescent screen are provided. Unitary screen-silver halide emulsion materials for X-ray recording have been described e.g. in the United States Patent Specification 2,887,379.

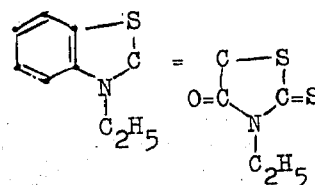
The emulsions may be spectrally sensitized by any of the known procedures. They may be spectrally sensitized by means of common spectrally sensitizing dyes used in silver halide emulsions, which include cyanine dyes and merocyanine dyes as well as other dyes as described by F. M. Hamer in "The Cyanine Dyes and related Compounds", Interscience Publishers (1964). These dyes are preferably used in an amount in the range of 20 mg to 250 mg per mole of silver halide.

Suitable spectral sensitizing dyes for silver halide to be used in the combination with screens emitting light

in the wavelength range of 480 - 600 nm are listed for illustrative purposes in the following table 2.

Table 2

1.



2.

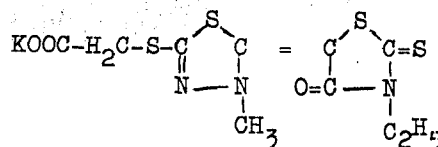
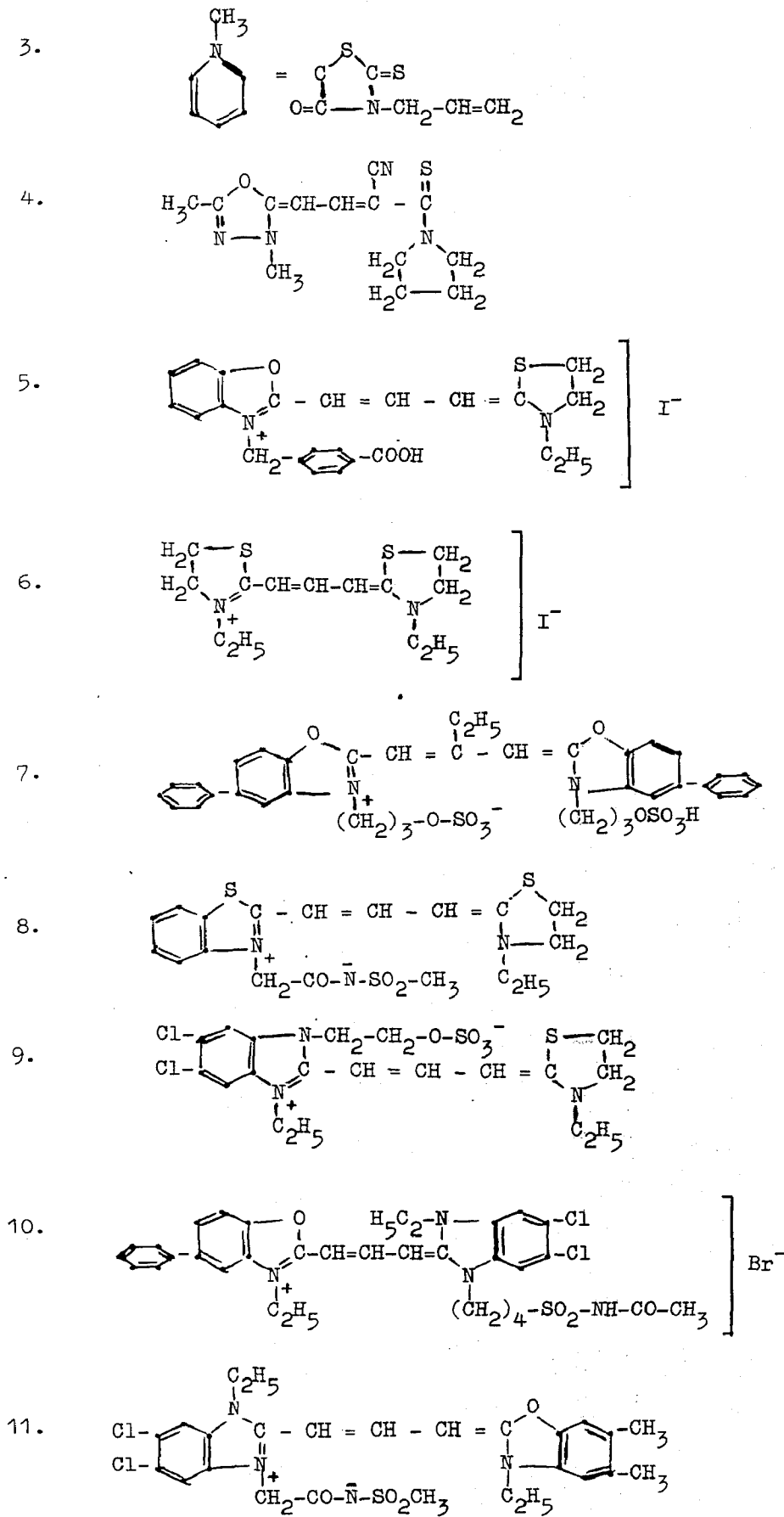
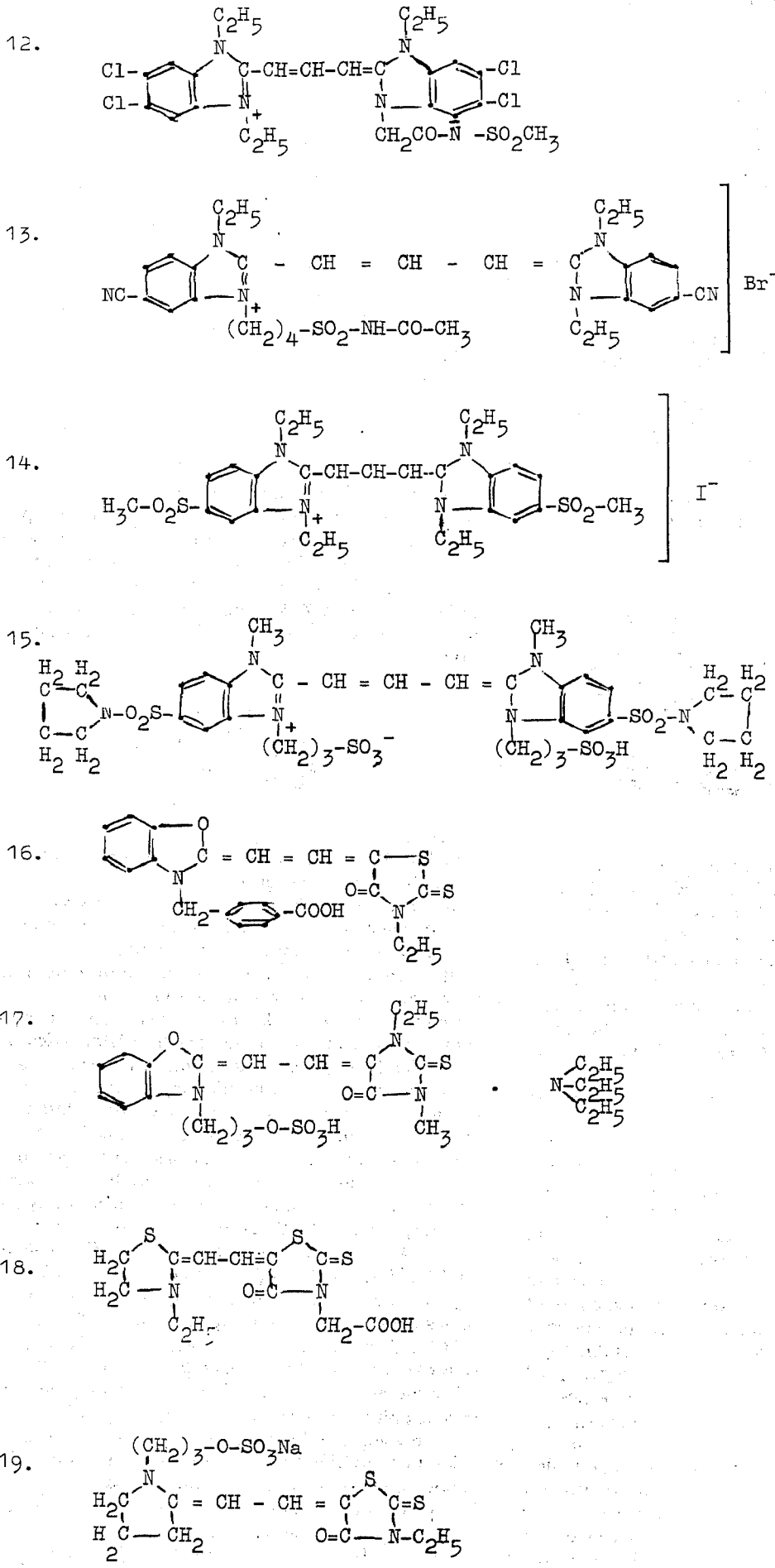
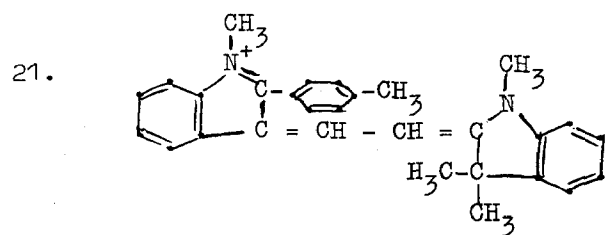
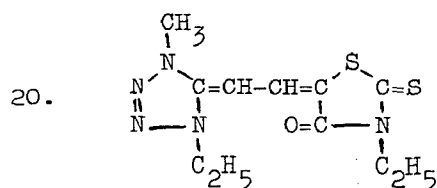


TABLE 2—Continued

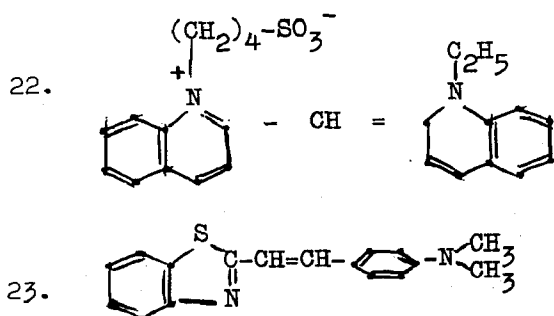








Supersensitization in the green spectral range may be obtained with the following compounds 22 and 23 of Table 2 in a molar ratio 1:2.

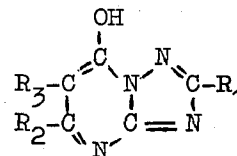


The silver halide in the emulsion layer(s) may comprise varying amounts of silver chloride, silver iodide, silver bromide, silver chlorobromide, silver bromoiodide, and the like, but when coated must be capable, after exposure and processing, of producing a negative silver image remaining thereon, i.e., in situ. Particularly good results are obtained with silver bromoiodide emulsions in which the average grain size of the silver bromoiodide crystals is in the range of about 0.1 to about 3 microns.

The image-forming silver halide emulsion may be chemically sensitized by any of the known procedures. The emulsions may be digested with naturally active gelatin or with small amounts of sulphur-containing compounds such as allyl thiocyanate, allylthiourea, sodium thiosulphate, etc. The image-forming emulsion may be sensitized likewise by means of reductors, e.g., tin compounds as described in the United Kingdom Pat. No. 789,823, polyamines e.g., diethyltriamine, and small amounts of noble metal compounds such as of gold, platinum, palladium, iridium, ruthenium, and rhodium as described by R. Koslowsky, Z.Wiss.Phot. 46, 67-72 (1951). Representative examples of noble metal compounds are ammonium chloropalladate, potassium chloroplatinate, potassium chloroaurate and potassium aurithiocyanate.

Emulsion stabilizers and antifoggants may be added to the silver halide emulsion before or after admixture of the low-speed emulsion, e.g., the known sulphinic and selenic acids or salts thereof, aliphatic, aromatic or heterocyclic mercapto compounds or disulphides, e.g.,

those described and claimed in published German Pat. No. 2,100,622, preferably comprising sulpho groups or carboxyl groups, mercury compounds e.g., those described in Belgian Pat. No. 524,121 - 677,337 - 707,386 and 709,195 and tetra-azaindenes as described by Birr in Z.Wiss.Phot. 47, 2-58 (1952), e.g., the hydroxy tetraazaindenes of the following general formula:



wherein:

each of R<sub>1</sub> and R<sub>2</sub> represents hydrogen, an alkyl, an aralkyl, or an aryl group, and

R<sub>3</sub> represents hydrogen, an alkyl, a carboxy, or an alkoxy-carbonyl group, such as 5-methyl-7-hydroxy-s-triazolo[1,5-a]-pyrimidine.

Other additives may be present in one or more of the hydrophilic colloid layers of the radiation-sensitive silver halide elements of the present invention, e.g., hardening agents such as formaldehyde, dialdehydes, hydroxy aldehydes, mucchloric and mucobromic acid, acrolein, and glyoxal, mordanting agents for anionic colour couplers or dyes formed therefrom, plasticizers and coating aids e.g., saponin, e.g., dialkylsulphosuccinic acid salts such as sodium diisooctylsulphosuccinate, alkylaryl polyether sulphuric acids, alkylaryl polyethersulphonic acids, carboxyalkylated polyethyleneglycol ethers or esters as described in French Pat. No. 1,537,417 such as iso-C<sub>8</sub>H<sub>17</sub>-C<sub>6</sub>H<sub>4</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>8</sub>OCH<sub>2</sub>COONa, fluorinated surfactants e.g., those described in Belgian Pat. No. 72,680 and the published German Patent Applications 1,950,121 and 1,942,665, inert particles such as silicon dioxide, glass, starch and polymethylmethacrylate particles.

For the purpose of accelerating the development, the exposed photographic material is developed preferably in the presence of development accelerators. These development accelerators can be used either in the silver halide emulsion, in adjacent layer(s) or in the developing bath. They include alkylene oxide compounds of various types, e.g., alkylene oxide condensation products or polymers as described in U.S. Pat. Nos.

1,970,578 — 2,240,472 — 2,423,549 — 2,441,389 — 2,531,832 and 2,533,990 and in United Kingdom Pat. Nos. 920,637 — 940,051 — 945,340 — 991,608 and 1,015,023. Other development accelerating compounds are onium and polyonium compounds preferably of the ammonium, phosphonium, and sulphonium type for example trialkyl sulphonium salts such as dimethyl-n-nonyl sulphonium p-toluene sulphonate, tetraalkyl ammonium salts such as dodecyl trimethyl ammonium p-toluene sulphonate, alkyl pyridinium and alkyl quinolinium salts such as 1-m-nitrobenzyl quinolinium chloride and 1-dodecylpyridinium chloride, bis-alkylene pyridinium salts such as N,N'-tetramethylene bispyridinium chloride, quaternary ammonium and phosphonium polyoxyalkylene salts especially polyoxyalkylene bispyridinium salts, examples of which can be found in U.S. Pat. No. 2,944,900, etc.

After radiographic exposure the radiographic silver halide elements of the present invention are developed, preferably in an energetic surface developer. The high energy is required in order to allow the development to proceed quickly and may be obtained by properly alkalinizing the developing liquid (pH 9–12), by using high-energy developing substances or a combination of developing substances, which as a consequence of their superadditive action is very energetic.

Economy on the silver halide in the emulsion is realized by building up the image density partly with dyes. Such may proceed by introducing (a) colour coupler(s) into the emulsion, which at least at the stage of the development form(s) (a) dye(s) with the oxidation product of an aromatic primary developing agent, e.g., of the p-phenylenediamine type, which dye(s) absorb(s) in the visible part of the spectrum.

Further it is known that a relatively high maximum density and contrast can be obtained even with a low amount of silver halide content per unit of surface when a colour image is produced together with a silver image as is described, e.g., in the published German Pat. No. (D.O.S.) 1,946,652.

It is further known that fine-grained silver halide emulsions have a higher covering power than coarse-grained emulsions (ref. P. Glafkides, *Photographic Chemistry*, Vol. I (1958) 89–90).

By the term "covering power" is understood the reciprocal of the photographic equivalent of developed silver, i.e., the number of grams of silver per sq. decimeter divided by the maximum optical density.

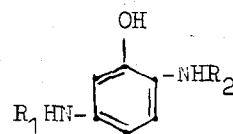
Fine-grained emulsions have a lower photographic speed. The low speed of said fine-grained emulsions having a high covering power e.g., at least 50, and low silver halide content, e.g., less than 80 mg of silver per sq.dm, may be compensated by the use of fluorescent screens containing fluorescent gadolinium compounds and having a particularly high intensification factor.

When applying a colour development preferably so-called 2-equivalent couplers are used to further reduce the consumption of silver thus only 2 instead of 4 molecules of exposed silver halide are necessary 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 therefor e.g., the U.S. Pat. No. 3,006,759). The density of the image is thus realized by addition of the densities of the silver image(s) combined with the dye image(s).

For improving the information content retrieval

those phenol or  $\alpha$ -naphthol type colour couplers are particularly suitable that on colour development of the silver halide with an aromatic primary amino developing agent form a quinoneimine dye mainly absorbing in the red and also absorbing in the green and having an absorption maximum in the spectral wavelength range of 550 to 700 (ref. therefor is made e.g., to the published German Patent Application D.O.S. No. P 1,946,652.)

Phenol couplers suited for that purpose correspond, e.g., to the following general formula:



wherein:

each of  $R_1$  and  $R_2$  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, a 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 types of phenol colour couplers and their preparation reference may be made to U.S. Pat. No. 2,772,162 and 3,222,176, to United Kingdom Pat. No. 975,773.

When colour images are prepared together with silver images, use is made of aromatic primary amino colour developing agents e.g., N,N-dialkyl-p-phenylenediamines and derivatives thereof, e.g., N,N-diethyl-p-phenylenediamine, N-butyl-N-sulphobutyl-p-phenylenediamine, 2-amino-5-diethylaminotoluene hydrochloride, 4-amino-N-ethyl-N( $\beta$ -methane sulphonamidoethyl)-m-toluidine sesquisulphate monohydrate and N-hydroxy-ethyl-N-ethyl-p-phenylenediamine. The colour developer can be used together with black-and-white developing agents e.g., 1-phenyl-3-pyrazolidinone and p-monomethylaminophenol which are known to have a superadditive effect on colour development (see L. F. A. Mason, *J. Phot. Sci.* 11 (1963) 136–139), and other p-aminophenol derivatives, e.g. those according to French Pat. No. 1,283,420 such as 3-methyl-4-hydroxy-N,N-diethylaniline, 3-methyl-4-hydroxy-N-ethyl-N- $\beta$ -hydroxyethylaniline, 1-methyl-6-hydroxy-1,2,3,4-tetrahydroquinoline, 1- $\beta$ -hydroxyethyl-6-hydroxy-1,2,3,4-tetrahydroquinoline, N-(4-hydroxy-3'-methylphenyl)-pyrrolidine, etc. It is also possible to use combinations of aromatic primary amino colour developing agents to obtain an increased rate of colour development (see e.g., German Pat. No. 954,311 and French Pat. No. 1,299,899); favourable effects are obtained e.g. by the use of N-ethyl-N-2-hydroxyethyl-p-phenylenediamine together with N-butyl-N-sulphobutyl-p-phenylenediamine, 2-amino-5-diethylamino-toluene hydrochloride or N,N-diethyl-p-phenylenediamine hydrochloride.

The developing solutions may also comprise any of the usual additional ingredients e.g., sodium sulphite

and hydroxylamine or derivatives thereof, hardening agents, antifoggants e.g., benzotriazole, 5-nitro-benzimidazole, 5-nitro-indazole, halides such as potassium bromide, silver halide solvents, toning and intensifying compounds, solvents e.g., dimethylformamide, dimethylacetamide and N-methyl-pyrrolidone for chemical ingredients that are difficult to dissolve in the preparation of the developing solutions or that tend to precipitate upon standing, etc.

The radiation-sensitive emulsions for use in the present invention may be coated on a wide variety of supports e.g., films of cellulose nitrate, cellulose esters, polyvinylacetal, polystyrene, polyethylene terephthalate and other polyester materials as well as  $\alpha$ -olefin-coated papers e.g., paper coated with polyethylene or polypropylene.

Preferred supports comprise a linear condensation polymer, polyethylene terephthalate being an example thereof.

The supports used in the present recording materials may be coated with subbing layers for improving the adhesion of (a) gelatino-silver halide emulsion layer(s) thereto. As already mentioned the support may be coloured. According to the present invention blue dyes are preferred. Blue polyester resin supports are known from the prior art.

The mechanical strength of melt-extruded supports of the polyester type can be improved by stretching. In some cases as described in the United Kingdom Pat. No. 1,234,755 the support may carry a subbing layer in the stretching stage.

Suited subbing layers are known to those skilled in the art of silver halide photography. With regard to the use of hydrophobic film supports reference is made to the composition of subbing layers described in the United Kingdom Pat. No. 1,234,755.

According to said specification a hydrophobic film support has (1) a layer which is directly adherent to the said hydrophobic film support and comprises a copolymer formed from 45 to 99.5% by weight of at least one of the chlorine-containing monomers vinylidene chloride and vinyl chloride, from 0.5 to 10% by weight of at least an ethylenically unsaturated hydrophilic monomer, and from 0 to 54.5% by weight of at least one other copolymerizable ethylenically unsaturated monomer; and (2) a layer comprising in a ratio of 1:3 to 1:0.5 by weight a mixture of gelatin and a copolymer of 30 to 70% by weight of butadiene with at least one copolymerizable ethylenically unsaturated monomer.

The exposed radiographic elements of the present invention are preferably processed in an automatic processing apparatus as is used for X-ray films in which the photographic material may be guided automatically and at a constant speed from one processing unit to the other, but it will be understood by those skilled in the art that the radiographic image recording elements disclosed herein can also be processed apart from the above mentioned automatic processing apparatus in a variety of ways, such as by using the manual conventional multi-tank methods well known in the art.

For common emulsion preparation processes and the use of particular emulsion ingredients reference is made in general to the Product Licensing Index of December 1971 in which the following terms are dealt with in more details:

I/II	Emulsion type and preparation of said element
III	Chemical sensitization
IV	Development modifiers
V	Antifoggants and stabilizers
VI	Developing agents
5 VII	Hardeners
VIII	Binding agents or polymers for silver halide layers and other layers
IX	Antistatic layers
X	Supports
XI	Plasticizers and lubricants
10 XII	Coating aids
XV	Spectral sensitization agents for silver halides
XXIII	Colour material ingredients
XVI	Absorbing and filter dyes
XXI	Physical development systems, and
15 XVII and XVIII	Addition agents and coating procedures.

The present invention includes the use of fluorescent gadolinium compounds in all types of neutron detection, neutron energy conversion and neutron image recording. A very interesting use of said fluorescent compounds lies in the conversion of neutron energy into visible light in image-intensifier tubes and in so-called neutron-ray image converters in analogy with X-ray image converters e.g., as described in the U.S. Pat. Nos. 3,403,279 and 3,617,743.

The structure of the neutron-ray image converter is basically the same as that of the X-ray image converter.

In such neutron-ray image converter the neutron energy conversion in fluorescent electromagnetic radiation takes place in a vacuum or reduced pressure photo-electron producing tube containing said neutron-absorbing screen in contact or optically coupled e.g., with fiber optics or lens system with a photocathode the image-wise emitted photo-electrons of which are electrically and/or magnetically focused to strike a luminescent cathode-ray sensitive screen. The neutron image is thus first converted in a fluorescent light image which is transformed with all its variations in luminance, into an "electron image" with similar variations in density. The acceleration of the electrons in the focusing electric field brings about essentially an intensification of the total "light" flux. In other words the greater the kinetic energy these electrons possess when impinging upon the cathode luminescent screen the more light they release. Therefore these tubes are also called "image-intensifier tubes."

Suitable X-ray image conversion or intensifier tubes using gadolinium containing rare earth oxysulfide phosphors and that can be used in neutron image conversion according to the present invention have been described by S. P. Wang et al. in IEEE Nuclear Science Transactions (1970), February, 49-56.

The fluorescent gadolinium compounds are suitable for the detection of neutrons of any energy content e.g. for the detection of "cold" neutrons (< 0.01 eV), "thermal" neutrons (0.01-0.5 eV), "epithermal" neutrons (0.5 eV - 10 keV), "fast" neutrons (> 10 keV).

The fluorescent gadolinium compounds normally contain 15.68 % of the gadolinium isotope Gd 157, which isotope is the most effective neutron absorber known. The higher the content of that isotope in the fluorescent compound the higher the neutron absorption.

According to a preferred embodiment the fluorescent gadolinium compounds contain gadolinium that is characterized by a higher Gd 157 content than 15.68 %, thus contain so-called isotope 157 enriched gadolinium.

The invention is illustrated in the drawing where a neutron image recording material comprising a support 1 covered with an anti-reflection layer 2 which contains a screening dye 6 dispersed in a binder 7 is coated with a fluorescent layer 3 containing a fluorescent substance 4 dispersed in a binder 5 with particular reference to the following example.

#### Example

Preparation of the light-sensitive silver halide material I used in the comparative test as described herein-after with the "standard gadolinium metal screen."

A silver bromoiodide X-ray emulsion (2 mole % of silver iodide) was prepared in such a way that it contained silver halide grains with an average grain size of  $0.4 \mu$  and comprised per kg an amount of silver halide corresponding to 190 g of silver nitrate and 74 g of gelatin.

As stabilizing agents the emulsion contained per kg 545 mg of 5-methyl-7-hydroxy-s-triazolo[1,5-a]pyrimidine, 6.5 mg of 1-phenyl-5-mercaptotetrazole, and 0.45 mg of mercury cyanide.

The above emulsion was coated on one side of a subbed polyethylene terephthalate support in such a way that on the support a silver halide emulsion layer was obtained containing an amount of silver halide equivalent to 12.5 g of silver nitrate per sq.m.

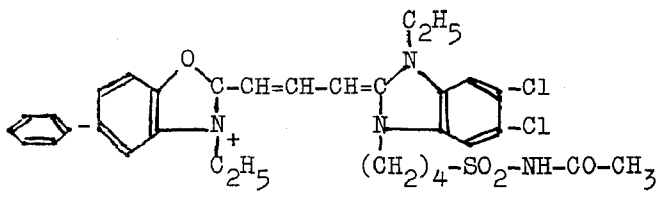
The emulsion layer was coated with a gelatino antistress layer at a coverage of 1 g/m<sup>2</sup>.

The above defined silver halide emulsion material was made with the object to obtain a recording material with optimum sensitivity for  $\beta$ -rays.

Preparation of the light-sensitive silver halide material II used in the comparative test as described herein-after with the "fluorescent gadolinium compound screen."

A silver bromoiodide X-ray emulsion (2 mole % of silver iodide) was prepared in such a way that it contained silver halide grains with an average grain size of  $1.25 \mu$  and comprised per kg an amount of silver halide corresponding to 190 g of silver nitrate and 74 g of gelatin.

The obtained silver halide emulsion was spectrally sensitized for light in the wavelength range of 480-600 nm with 150 mg per kg emulsion of a spectral sensitizing dye corresponding to the following structural formula:



As stabilizing agents the emulsion contained per kg 545 mg of 5-methyl-7-hydroxy-s-triazolo[1,5-a]pyrimidine, 6.5 mg of 1-phenyl-5-mercaptotetrazole, and 0.45 mg of mercury cyanide.

The above emulsion was coated on one side of a subbed polyethylene terephthalate support in such a way that on the support a silver halide emulsion layer was obtained containing an amount of silver halide equivalent to 7 g of silver nitrate per sq.m.

The emulsion layer was coated with a gelatino antistress layer at a coverage of 1 g/m<sup>2</sup>.

Composition of the "standard screen" (metal screen for use in the "direct method").

The "standard screen" is a gadolinium metal foil with a thickness of 20 microns.

Composition of the fluorescent screen material used according to the present invention in the "direct method."

The fluorescent screen is composed of a fluorescent layer applied onto a polyethylene terephthalate resin support having a thickness of 250 microns.

The fluorescent layer contains dispersed in a binder Gd<sub>2</sub>O<sub>3</sub>S activated with 0.3 % (calculated on the gadolinium) of terbium. The fluorescent layer is applied to an antihalation layer containing 5 mg per sq.m of the dye NEOZAPON FIRE RED (C.I. Solvent Red 119) in a binder adhering to the polyester.

The fluorescent particles have an average grain size of 10 microns and are applied at a coverage of 390 grams per sq.m. The thickness of the fluorescent screen is 101 microns.

The fluorescent layer is covered with a resin type antistress layer of 15 microns.

Exposure ("direct method").

A thermal neutron beam was emitted from the nuclear reactor through a monocrystal of copper. Operating that way a beam of "monochromatic" neutrons ( $\lambda = 0.1065 \text{ nm}$ ) of a flux of  $4.10^5$  neutrons per sq.cm per sec. was obtained for the exposure. The  $\gamma$ -ray intensity in that beam was 300 milliroentgen (mr) per hour.

Both light-sensitive silver halide emulsion materials were under the same circumstances exposed with that "monochromatic" neutron beam through a test object. The test object was an iron step wedge containing three steps (total height of the three steps = 12.7 mm) having on each step small objects of different size, form and neutron absorption coefficient (ref. British Journal of Applied Physics, 7 (October 1956) (page 346)) viz. objects of Fe, Cd, In, Gd, polyamide, Pb and Dy.

The above described "standard screen" and the gadolinium oxysulphide screen were during the exposure to the test object held in contact respectively with the silver halide emulsion layer of silver halide material I and II.

Test object images with same average optical density were obtained by using for the combination of the "standard screen" and the silver halide material I a dosis of  $4.2 \times 10^8$  neutrons per sq.cm and for the combination of the fluorescent gadolinium compound

screen with the silver halide material II only  $1.7 \times 10^7$  neutrons per sq.cm so that the last mentioned combination may be considered as being about 250 times more sensitive for neutron detection and recording than the combination containing the "standard screen."

In a further test carried out according to the "transfer method" a dysprosium screen was used as converter screen that becomes radioactive and  $\beta$ -ray emitting after neutron bombardment. The dysprosium screen was exposed with a neutron dosis of  $3.6 \times 10^{10}$  neutrons per sq.cm.

The thus exposed dysprosium screen was 18 min after the neutron irradiation kept for 3 hours in direct

contact with the above described silver halide emulsion layer of material I. The obtained optical density was the same as the one obtained in the "direct method" with the silver halide material II combined with the gadolinium oxysulphide screen which received, however, a neutron dosis being 2,000 times smaller than the above neutron dose applied onto the dysprosium screen.

We claim:

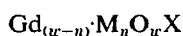
1. A method of recording neutron images which method comprises the steps of (1) information-wise irradiating with neutrons an intensifying screen incorporating a phosphor compound in which gadolinium is the host metal and at least one other rare earth metal is present as a fluorescence activating metal; and (2) subjecting the fluorescent light pattern resulting from the impact of the neutrons on the screen onto a photographic material.

2. A method according to claim 1, wherein the gadolinium host metal is an oxide, oxyhalide or oxysulphide of gadolinium.

3. A method according to claim 1 wherein the gadolinium host metal is gadolinium oxysulphide or gadolinium oxyhalide.

4. A method according to claim 3, wherein the activating metal is at least one of the metals of the group consisting of terbium, dysprosium, erbium, europium, holmium, neodymium, praseodymium, samarium, thulium and ytterbium.

5. A method according to claim 1, wherein the gadolinium host metal corresponds to the following general formula:



wherein:

M is at least one of the metals terbium, dysprosium, erbium, europium, holmium, neodymium, praseodymium, samarium, thulium or ytterbium,

X is sulphur or halogen,

n is 0.0002 to 0.2, and

w is 1 when X is halogen or is 2 when X is sulphur.

6. A method according to claim 1, wherein the gadolinium host metal is gadolinium oxysulphide activated with terbium.

7. A method according to claim 1, wherein the gadolinium host metal contains gadolinium with a Gd 157 isotope content larger than 15.68 %.

8. A method according to claim 1, wherein the intensifying screen is in the form of a layer applied to a support or is a self-supporting layer or sheet.

9. A method according to claim 8, wherein the layer or sheet contains the gadolinium host metal in the form of particles dispersed in a binder.

10. A method according to claim 9, wherein said particles have a size in the range of 1 to 20 microns.

11. A method according to claim 9, wherein the layer has a thickness of 10 to 300 microns.

12. A method according to claim 9, wherein the binder is present in said layer in a proportion of 5-15 % by weight with respect to the fluorescent material.

13. A method according to claim 1, wherein the in-

tensifying screen including said phosphor compound is used in conjunction with another neutron-absorbing screen of the group of metallic, glassy or granular type screens.

14. A method according to claim 1, wherein the intensifying screen is used in conjunction with a metal screen that becomes radioactive by neutron bombardment.

15. A method according to claim 1, wherein the intensifying screen is used in conjunction with a metal screen having a neutron absorption coefficient at least as high as lithium.

16. A method according to claim 1, wherein the photographic material includes a photosensitive silver halide emulsion layer coated on a support.

17. A method according to claim 1, wherein the photographic material includes a silver halide emulsion layer on each side of a support.

18. A method according to claim 16, wherein said photographic material contains a filtering dye or dyes improving the sharpness of the silver image obtainable in said material.

19. A method according to claim 18, wherein said dye or dyes have such chemical and physical characteristics that they can be removed or decolourized in one of the processing baths used for the photosensitive silver halide material.

20. A method according to claim 18, wherein said dye or dyes are incorporated in a hydrophilic colloid layer.

21. A method according to claim 20, wherein the dye or dyes are incorporated in a hydrophilic colloid layer between the silver halide emulsion layers when using a material with duplitzed coating or in the silver halide emulsion layers themselves.

22. A method according to claim 18, wherein the dye or dyes are incorporated in one or more subbing layers or in an antihalation layer at either side of the support.

23. A method according to claim 18, wherein the dye or dyes are present in the support.

24. A method according to claim 16, wherein the intensifying screen and the photo-sensitive silver halide material form an integral arrangement.

25. The method of claim 16, wherein the intensifying screen is arranged separately from the photo-sensitive material containing the silver halide.

26. A method according to claim 16, wherein the silver halide has been spectrally sensitized.

27. A method according to claim 16, wherein the silver halide is a silver bromoiodide having an average grain size in the range of about 0.1 to 5  $\mu$ .

28. A method according to claim 16, wherein the silver halide emulsion layer(s) contain(s) a colour coupler for forming a dye with an oxidized p-phenylenediamine developing agent.

29. A method according to claim 16, wherein the photosensitive silver halide material contains an amount of silver halide equivalent to above 3 to 8 g silver per sq.m.

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