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3,235,728 COLOR RADIOGRAPHY

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A 36,927 4 Claims. (Cl. 250—65)

This invention relates to a process for the production of color radiographs as well as to a light-sensitive material for performing the said process.

To observe objects which are not visible to the eye, use is frequently made in medicine and industry of the 15 process of producing photographic images of these objects by means of δ-rays, X-rays or other penetrating actinic rays. A major disadvantage of the silver halide emulsions used for such radiographic materials is their Only films of highest possible sensitivity and thus of low resolving power are consequently considered to be suitable for the instant purpose. Furthermore, another disadvantage of X-ray exposures is caused by the low differences in the transparencies of the different parts of the 25 tice, whereby a two-colored radiograph is obtained. objects to the X-rays. This leads to low contrasts in the resulting radiographic image. The relatively thick emulsion layers necessary for producing a negative having a sufficient contrast reduce considerably the distinctness or clarity of the details of the resulting image. The same 30 disadvantageous effect is caused by the intensifier foils used for increasing the sensitivity.

It has already been proposed to improve the discernibility of the details of X-ray images, which is normally very low, by transforming the silver image into a dye- 35 stuff image.

Because color contrasts can be detected by the eye better than black-and-white contrasts the improvement in the distinctness of the details of the image can also be achieved by using a two-layer material containing dye- 40 stuff components. With this process, the Hurter and Driffield (H & D) curve of the two color layers must be of different steepness. In this case however small exposure contrasts do not produce large color contrasts.

It is also known to produce a two-color X-ray picture 45 by using two couplers in the light-sensitive layer, these couplers having different coupling speeds and producing coupling products of different colors. It is true that this process supplies two-color X-ray pictures having improved distinctness of detail, but it is disadvantageous to the ex- 50 tent that it requires certain combination of two color couplers, which must be exactly matched to one another. The discovery of such a pair of couplers presents considerable difficulties.

It is among the objects of the present invention to 55avoid the disadvantages described above and to provide a film material which is eminently suitable for the preparation of X-ray images having an excellent contrast and a high distinctness of the details of the image.

The objects of the invention can be attained by using 60 a film material comprising a support and two light-sensitive silver halide emulsion layers containing different color couplers which yield dyestuffs of different color by development with a suitable color-forming primary aromatic amine developer. The two layers can be arranged one 65 tion thereto. above the other on the same side or separately, one on each of the two sides of the support. Such a material can be built up, for example, as follows:

A support consisting, for example, of a cellulose ester carbonate, particularly a polycarbonate of a bis(hydroxyphenyl)alkane, a polyester derived from ethylene glycol

and terephthalic acid, paper or glass, is coated with a silver halide emulsion layer that is sensitized to yellow light containing a cyan color coupler. Above this layer is cast another silver halide emulsion layer that is not additionally sensitized containing a red color coupler.

The imagewise exposure of the film material is effected in conventional manner, for example, by means of X-rays. The sensitivity of the material can be increased in conventional manner by the use of luminescent screens or by fluorescing substances embedded in the emulsions or by intensifier foils. The exposed material is developed in conventional manner by means of a color-forming primary aromatic amine developer, for example, in accordance with the general procedure of the Agfacolor negativepositive process. Thereafter the developed material containing congruent silver and dyestuff images is subjected to a second, non-imagewise exposure to light of the yellow region of the visible spectrum. This is preferably performed by exposing the film through a yellow filter, for low sensitivity with respect to X-rays or similar radiation. 20 example, the Agfa dark-room filter 112 or the Agfa Repro color separation filter L4.

The second exposure is followed by a second development. Further processing of the exposed and developed material is performed in accordance with common prac-

The object of the subsequent non-imagewise exposure with yellow light is to expose the yellow-sensitive layer at the areas which have remained unexposed during the imagewise exposure. The unsensitized layer exposed to light during the first exposure remains unaffected by the subsequent non-imagewise exposure with yellow light. The silver and dyestuff images of the first imagewise exposure which are formed in this layer during the first development act as a black filter at the subsequent exposure to yellow light and prevent a second exposure of the yellow-sensitive layer at the areas which had been affected by the first imagewise exposure.

In accordance with one specific form of the invention the layers of different sensitivity and containing different color couplers are arranged separately on the two sides of the support. With such a material, a subsequent influencing of the two-colored layers is possible. The subsequent exposure when using this material is of course effected from the side of the film where the silver halide emulsion layer insensitive to the light rays of the subsequent exposure is arranged.

By suitable matching of the sensitivities of the two layers relative to each other when manufacturing the material and furthermore by suitable proportioning of the second exposure with yellow light in the processing, a darker carmine-red image is obtained in relation to a light bluish-green background. The dark areas of a conventional X-ray image are therefore transformed into a relatively dark red, while the light areas are changed into a relatively light bluish-green, thereby obviating a "mental reversal" in the evaluation of the radiograph with respect to the hitherto usual method of examining a negative image, it being known that such a mental reversal is always greatly resisted. The process also makes it possible for a positive X-ray image to be produced by simple variation of the subsequent light exposure.

The following examples will illustrate our invention, it being understood that these examples represent embodiments but are not to be considered as limiting the inven-

# Example 1

A transparent cellulose acetate foil provided with a subbing layer is coated with a silver chloride gelatin such as a cellulose acetate or cellulose nitrate film, a poly- 70 emulsion which is panchromatically sensitized and contains 10 g. of the sodium salt of 1-hydroxy-2-naphthoylamino-4'-(methylheptadecylamino)benzene - 3' - sulfonic

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acid having Formula I hereinafter, per kilogram. Onto this layer is cast a silver bromide gelatin layer which is not additionally sensitized containing 10 g. of N-(2-methyloctadecylamino-5-carboxyphenyl) - 4 - hydroxyethoxybenzoylacetamide having the Formula II hereinafter, per kilogram. Said film is exposed to X-rays in conventional manner by interposing the object to be radiographed between said film and the X-ray source. The exposed film is developed by means of an alkaline developer containing N,N-dimethylphenylene diamine as the color-forming developer compound at 20° C. for 8 minutes.

The second exposure is accomplished through a yellow filter (Agfa Repro color separation filter L4—exposure time 30 seconds). Thereafter it is developed again in a 15 developer described above. Finally the developed film is bleached and fixed after washing and drying. The resulting radiograph shows a yellow dyestuff image of the object. The background of the image has a cyan color.

#### Formula I

#### Formula II

# Example 2

A transparent foil formed of a polycarbonate of a bis-(hydroxyphenyl) alkane is coated on one side with a silver chloride gelatin emulsion layer containing the cyan coupler represented by Formula I hereinbefore in Example 1. The opposite side of the support is coated with a silver bromide gelatin emulsion layer which is not additionally sensitized containing 10 g. of  $\omega$ -(p-dodecylaminobenzylidene)- $\omega$ -cyano-acetone having Formula III hereinafter and 10 g. of the sodium salt of dodecyl sulfate ( $C_{12}H_{25}OSO_3Na$ ). The film is processed as described in Example 1 whereby the second exposure with yellow light is effected from the side of the film carrying the silver bromide emulsion layer. A magenta image on a cyan colored background is obtained.

### Formula III

Having thus described our invention we now state that we believe our invention to be capable of numerous variations in method and materials; for example, the processs according to the invention is not restricted to the color combination of the resulting two-colored radiograph image because it may comprise any suitable combination allowing a high distinctness of the details. The inventive process can be performed with any color photographic material containing at least two color couplers forming upon color-forming development differently colored dyestuffs. The color component can be arranged in two or more layers as well as in a single layer consisting of a so-called mixed-grain emulsion.

The chemical structure of the color coupler to be used

is not especially critical but is selected according to the requirements of the particular radiographic process.

The development can be performed with any colorforming developer, for instance, a primary aromatic amine developer. Furthermore the subsequent exposure may be performed with any colored light of the visible spectrum for which one of the silver halide emulsions has been sensitized and can be performed during or after the first development. Bleaching and fixing of the developed film is performed in conventional manner.

We claim:

1. A process for producing a colored radiograph with X-rays comprising

- (a) exposing to said rays a light-sensitive radiographic material comprising two light-sensitive silver halide emulsion layers supported on a transparent supporting layer, the top emulsion layer of which contains no additional sensitizer and the lower emulsion layer is sensitized to yellow light, each of the emulsion layers being sensitized to different regions of the spectrum and containing different color couplers which upon development form dyestuffs of different color;
- (b) developing the said material with a color-forming developer, thereby forming a silver image and a dyestuff image at the light-struck areas, in each of said two emulsion layers;
- (c) subjecting the developed material to a second diffused, non-image-wise exposure to light in the yellow region of the visible spectrum to which only one of the emulsion layers is sensitive;
- (d) developing the said exposed material with a colorforming developer; and
- (e) subsequently bleaching and fixing the said developed material,

whereby a colored radiograph containing a colored-image on a differently colored background is produced.

- 2. A process as defined in claim 1 in which the lightsensitive radiographic material comprises a transparent supporting layer and two light-sensitive silver halide emulsion layers superimposed thereon.
- 3. A process as defined in claim 1 in which the lightsensitive radiographic material comprises a transparent supporting layer and two light-sensitive silver halide emulsion layers arranged on opposite sides of the supporting layer.
- 4. A process as defined in claim 1 in which the (a) step utilizes emulsion layers containing color couplers which upon development with a primary aromatic amine developer, form dyestuffs whose colors are complementary to each other.

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