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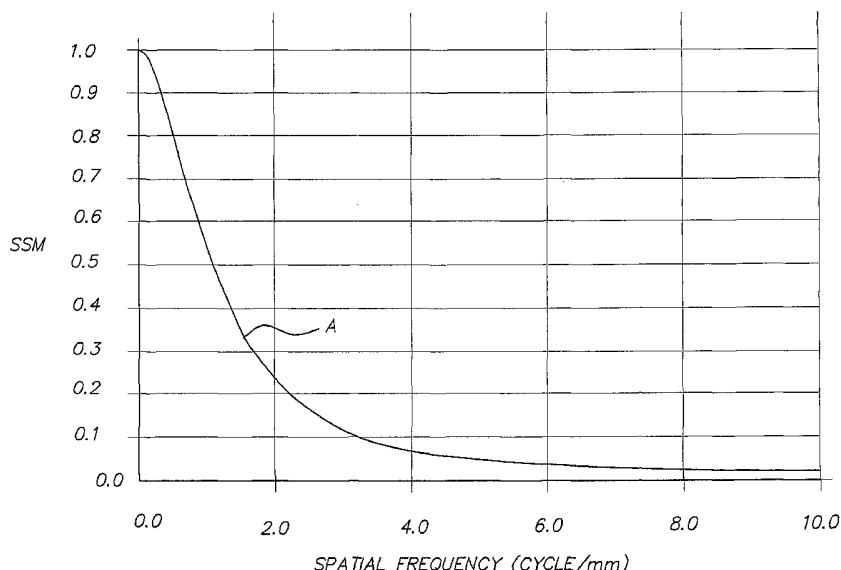
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(54) Title: ULTRAHIGH SPEED IMAGING ASSEMBLY FOR RADIOGRAPHY



(57) Abstract: A radiographic imaging assembly comprises a symmetric radiographic silver halide film has an overall system speed of at least 1100 to provide images with improved contrast and sharpness and reduced fog. The imaging assembly includes a symmetric radiographic film having a speed of at least 700 that includes at least two silver halide emulsions on each side of the support that comprise tabular silver halide grains. The emulsions closer to the support comprise a suitable crossover control agent. The imaging assembly also includes a pair of phosphor intensifying screens that have an average screen sharpness measurement (SSM) greater than reference Curve A of FIG. 4. The screens can have a support that includes a reflective substrate comprising a continuous polyester phase and microvoids containing inorganic particles dispersed within the polyester phase.

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## ULTRAHIGH SPEED IMAGING ASSEMBLY FOR RADIOGRAPHY

### FIELD OF THE INVENTION

This invention is directed to radiography. In particular, it is  
5 directed to a ultrahigh speed radiographic imaging assembly containing a  
radiographic silver halide film and fluorescent intensifying screens and that  
provides improved medical diagnostic images at reduced imaging dosage.

### BACKGROUND OF THE INVENTION

10 In conventional medical diagnostic imaging the object is to obtain  
an image of a patient's internal anatomy with as little X-radiation exposure as  
possible. The fastest imaging speeds are realized by mounting a dual-coated  
radiographic element between a pair of fluorescent intensifying screens for  
imagewise exposure. 5% or less of the exposing X-radiation passing through the  
15 patient is adsorbed directly by the latent image forming silver halide emulsion  
layers within the duplitized radiographic element. Most of the X-radiation that  
participates in image formation is absorbed by phosphor particles within the  
fluorescent screens. This stimulates light emission that is more readily absorbed  
by the silver halide emulsion layers of the radiographic element.

20 Examples of radiographic element constructions for medical  
diagnostic purposes are provided by U. S. Patents 4,425,425 (Abbott et al.)  
4,425,426 (Abbott et al.), 4,414,310 (Dickerson), 4,803,150 (Dickerson et al.),  
4,900,652 (Dickerson et al.), 5,252,442 (Tsaur et al.), and 5,576,156 (Dickerson),  
and *Research Disclosure*, Vol. 184, August 1979, Item 18431.

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### Problem to be Solved

Image quality and radiation dosage are two important features of  
film-screen radiographic combinations (or imaging assemblies). High image  
quality (that is high resolution or sharpness) is of course desired, but there is also  
30 the desire to minimize exposure of patients to radiation. Thus, "high speed"  
imaging assemblies are needed. However, in known imaging assemblies, the two

features generally go in opposite directions. Thus, imaging assemblies that can be used with low radiation dosages (that is, "high speed" assemblies) generally provide images with poorer quality (poorer resolution). Lower speed imaging assemblies generally require higher radiation dosages.

5                   Conventional radiographic film-screen combinations, known as imaging assemblies (or systems), useful for general radiography, may have a total system speed of up to 400 but lack sufficient crossover control. The use of higher speed films in such assemblies may not be useful because of a need to control fog or unwanted density in the non-imaged areas of the film.

10                   There is a need for high speed imaging assemblies that are useful especially for general-purpose radiography that require minimum radiation dosages with minimal sacrifice in image quality (for example, resolution or sharpness).

## 15                   SUMMARY OF THE INVENTION

This invention provides a radiographic imaging assembly that has a system speed of at least 800 and comprises:

A)       a symmetric radiographic silver halide film having a film speed of at least 700 and comprising a support that has first and second major  
20       surfaces,

the radiographic silver halide film having disposed on the first major support surface, two or more hydrophilic colloid layers including first and second silver halide emulsion layers, and having on the second major support surface, two or more hydrophilic colloid layers including third and fourth silver  
25       halide emulsion layers, the first and third silver halide emulsion layers being the outermost emulsion layers on their respective sides of the support,

the second and fourth silver halide emulsion layers comprising a crossover control agent sufficient to reduce crossover to less than 15%, and

B)       a fluorescent intensifying screen arranged on each side of  
30       the radiographic silver halide film, the pair of screens having a screen speed of at least 400 and the screens having an average screen sharpness measurement value

greater than reference Curve A of FIG. 4, and each screen comprising an inorganic phosphor capable of absorbing X-rays and emitting electromagnetic radiation having a wavelength greater than 300 nm, the inorganic phosphor being coated in admixture with a polymeric binder in a phosphor layer on a support.

5                   In preferred embodiments, the invention provides a radiographic imaging assembly having a system speed of at least 1100 and comprising:

                  A)     a symmetric radiographic silver halide film having a film speed of at least 800 and comprising a support that has first and second major surfaces,

10                   the radiographic silver halide film having disposed on the first major support surface, two or more hydrophilic colloid layers including first and second silver halide emulsion layers, and having on the second major support surface, two or more hydrophilic colloid layers including third and fourth silver halide emulsion layers, the first and third silver halide emulsion layers being the  
15     outermost emulsion layers on their respective sides of the support,

                  each of the first, second, third, and fourth silver halide emulsion layers comprising tabular silver halide grains that have the same composition, independently an aspect ratio of from 38 to 45, an average diameter of at least 3.5  $\mu\text{m}$ , and an average thickness of from 0.08 to 0.14  $\mu\text{m}$ , and comprise at least 95  
20     mol % bromide and up to 0.1 mol % iodide, both based on total silver in the grains,

                  each of the second and fourth silver halide emulsion layers comprising a particulate oxonol dye as a crossover control agent present in an amount of from 1 to 1.3  $\text{mg}/\text{m}^2$  that is sufficient to reduce crossover to less than  
25     12% and that is decolorized during development within 45 seconds,

                  the film further comprising a protective overcoat on both sides of the support disposed over all of the silver halide emulsion layers,

                  wherein the tabular silver halide grains in the first, second, third, and fourth silver halide emulsion layers are dispersed in a hydrophilic polymeric vehicle mixture comprising from 5 to 15% of deionized oxidized gelatin, based on  
30     the total dry weight of the polymeric vehicle mixture,

wherein the dry, unprocessed thickness ratio of the first silver halide emulsion layer to that of the second silver halide emulsion layer is from 3:1 to 1:1, and the dry, unprocessed thickness ratio of the third silver halide emulsion layer to that of the fourth silver halide emulsion layer is independently from 3:1 to 1:1, and

wherein the molar ratio of silver in the first silver halide emulsion layer to that of the second silver halide emulsion layer is from 1.5:1 to 3:1, and the molar ratio of silver in the third silver halide emulsion layer to that of the fourth silver halide emulsion layer is independently from 1.5:1 to 3:1, and

10 B) a fluorescent intensifying screen arranged on both sides of the film, the pair of screens having a screen speed of at least 600 and the screens having an average screen sharpness measurement (SSM) value that is at least 1.1 that of reference Curve A of FIG. 4 at a given spatial frequency, and each screen comprising a terbium activated gadolinium oxysulfide phosphor capable of  
15 absorbing X-rays and emitting electromagnetic radiation having a wavelength greater than 300 nm, the phosphor being coated in admixture with a polymeric binder in a phosphor layer on a flexible polymeric support.

This invention also provides a method of providing a black-and-white image comprising exposing the radiographic silver halide film in the  
20 radiographic imaging assembly of the present invention and processing the film, sequentially, with a black-and-white developing composition and a fixing composition. The resulting black-and-white images can be used for a medical diagnosis.

The present invention provides a means for providing general-  
25 purpose radiographic images having desired image quality using reduced imaging X-radiation dosage (perhaps up to 3 times reduction) because of the high system speed (at least 1100) provided by a unique combination of film and screen.

In addition, all other desirable sensitometric properties are maintained and the radiographic film of the imaging assembly can be rapidly  
30 processed in conventional processing equipment and compositions.

These advantages are achieved by using a novel combination of a high speed symmetric radiographic silver halide film (at film speed of at least 700) and a pair of fluorescent intensifying screens (a screen speed of at least 600) arranged on opposing sides of the film. The symmetric radiographic silver halide film has a set of two silver halide emulsion layers on both sides of the film support comprising tabular silver halide grains having specific halide compositions, grain sizes, and aspect ratios to achieve the desired film speed. In addition, the silver halide emulsion layers closest to the support on both sides comprise crossover control agents. In preferred embodiments, the tabular grains in all emulsion layers are dispersed in a hydrophilic polymer vehicle mixture that includes at least 0.05 weight % of oxidized gelatin (based on total dry weight of the hydrophilic polymer vehicle mixture). With the unique choice of fluorescent intensifying screen and radiographic film of this invention, images with increased sharpness can be obtained at high speeds (thus, at lower radiation dosage). Such image quality improvements can be characterized by screen SSM values being greater than the values represented by reference Curve A of FIG. 4 over the range of spatial frequencies. In some preferred embodiments, image quality improvements can be characterized by screen SSM values being greater than the values represented by reference Curve A of FIG. 5 over the range of spatial frequencies.

Further advantages are provided in preferred embodiments with a specific microvoided reflective substrate in the flexible support of the fluorescent intensifying screen used in the imaging assembly. Within the microvoids are suitable reflective inorganic particles, and especially particles of barium sulfate. As a result, this screen has increased reflectivity to electromagnetic radiation, especially radiation in the region of from 350 to 450 nm.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a simplified schematic representation of a test system used to determine SSM values.

FIG. 2 is a graphical representation of the X-radiation waveform obtained from a typical test system used to determine SSM values.

FIG. 3 is a graphical representation of a Fourier transform of data obtained from repetitions of X-radiation waveforms.

FIG. 4 is a graphical representation of SSM vs. spatial frequencies for the imaging assembly of the present invention described in the Example 1  
5 using Film C and Screen Y.

FIG. 5 is a graphical representation of SSM vs. spatial frequencies for the imaging assembly of the present invention described in the Example 2 using Film C and Screen V.

FIG. 6 is a graphical representation of SSM vs. spatial frequencies  
10 for the imaging assembly of the present invention described in the Example 3 using Film C and Screen X.

## DETAILED DESCRIPTION OF THE INVENTION

### Definition of Terms:

15 Unless otherwise indicated, the terms “radiographic imaging assembly” and “imaging assembly” refer to the embodiments of the present invention.

The term "contrast" as herein employed indicates the average contrast derived from a characteristic curve of a radiographic film using as a first  
20 reference point (1) a density ( $D_1$ ) of 0.25 above minimum density and as a second reference point (2) a density ( $D_2$ ) of 2.0 above minimum density, where contrast is  $\Delta D$  (i.e. 1.75)  $\div \Delta \log_{10} E$  ( $\log_{10} E_2 - \log_{10} E_1$ ),  $E_1$  and  $E_2$  being the exposure levels at the reference points (1) and (2).

“Gamma” is described as the instantaneous rate of change of a D  
25  $\log E$  sensitometric curve or the instantaneous contrast at any  $\log E$  value.

“System speed” refers to a measurement given to combinations (“systems” or imaging assemblies) of radiographic silver halide films and fluorescent intensifying screens that is calculated using the conventional ISO 9236-1:1996(E) standard wherein the radiographic film is exposed and processed  
30 under the conditions specified in Eastman Kodak Company’s Service Bulletin 30. In general, system speed is thus defined as 1 milliGray/ $K_s$  wherein  $K_s$  is Air

Kerma (in Grays) required to achieve a density =  $1.0 + D_{\min} + \text{fog}$ . In addition, 1 milliRoentgen (mR) is equal to 0.008732 milliGray (mGray). For example, by definition, if 0.0025 milliGray (equal to 0.286 mR) incident on a film-screen system creates a density of 1.0 above  $D_{\min} + \text{fog}$ , that film-screen system is  
5 considered to have a speed of “400”.

However, the ISO speed depends on the x-ray spectrum, and is different for the four ISO conditions. It is common to use a “scaled” version of system speed, wherein Radiographic Film A described below used in combination with a pair of fluorescent intensifying screens identified as “X” below, when  
10 exposed with an 80 kV (constant potential) X-ray spectrum, filtered with 0.5 mm copper and 1 mm aluminum, at an exposure duration of approximately 0.15 seconds, is assigned or designated a speed value of 400.

The ISO condition four speed for this system is approximately 500. Thus, the relationship between the ISO condition four speed value and the  
15 definition of system speed used in this application is approximately the ratio  $500/400 = 1.25$ . That is, the numerical values of the system speed in this application are 0.80 times those directly obtained using equation 7.1 of the noted ISO 9236-1:1996E) standard. Thus, the “scaled” system speed values are used in this application. However, they can be converted to ISO speed values by dividing  
20 them by 0.80.

In this application, “film speed” has been given a standard of “400” for Radiographic Film A described in Example 1 below, that has been exposed for approximately 0.15 second and processed according to conditions shown in Example 1, using a pair of fluorescent intensifying screens containing a terbium  
25 activated gadolinium oxysulfide phosphor (such as Screen “X” noted below). Thus, if the  $K_s$  value for a given system using a given radiographic film is 50% of that for a second film with the same screen and exposure and processing conditions, the first film is considered to have a speed 200% greater than that of the second film.

30 Also in this application, “screen speed” has been given a standard of “400” for a pair of screens identified below as Screen “X”, each screen

containing a terbium activated gadolinium oxysulfide phosphor. Thus, if the  $K_s$  value for a given system using a given screen pair with a given radiographic film is 50% of that for a second screen pair with the same film and exposure and processing conditions, the first screen pair is considered to have a speed 200% greater than that of the second screen pair.

The "screen speed" values noted herein are in reference to a pair of screens (either symmetric or asymmetric) arranged on opposing sides of a radiographic film.

The "screen sharpness measurement" (SSM) described herein is a parameter that has been found to correlate well with visual appearance of image sharpness if other conditions are held constant.

Each screen sharpness measurement described in this application was made using a test system that is described as follows as illustrated in FIG. 1. A slit-shaped X-ray exposure **10** was made onto phosphor screen sample **15** (in a front-screen configuration) that was in contact with optical slit **20**. The profile or spread **45** of the emitted light from the screen was determined by scanning optical slit **20** relative to X-ray slit (or mask) **25** and digitizing the resulting signal. Photomultiplier tube **30** (PMT) was used to detect the light that passed through optical slit **20**. Data processing was done during acquisition and analysis to minimize noise in the resulting light spread profile (LSP). A Fourier transform of the LSP was calculated to give the SSM as a function of spatial frequency.

In FIG. 1, a very narrow tungsten carbide mask (10-15  $\mu\text{m}$  wide, 0.64 cm thick, and 0.64 cm long) was used as X-ray slit **25** to provide slit-shaped X-ray exposure **10**. X-ray slit **25** was held fixed with respect to the source of X-radiation. Phosphor screen sample **15** was placed face down (exit surface) on top of optical slit **20** made of two pieces of sharpened tool steel. The steel had been darkened by a chemical treatment and further blackened by a black felt-tipped pen. Phosphor screen sample **15** was held in place by a piece of a carbon fiber cassette panel (not shown) that was held down by pressure from spring-loaded plungers (not shown). The light passed through optical slit **20** was collected by integrating sphere **35** and a fraction of it was then detected by PMT **30**. The whole assembly

of phosphor screen sample **15**, optical slit **20**, integrating sphere **35**, and PMT **30** was translated relative to X-ray slit **25**. Optical slit **20** was aligned with X-ray slit **25**. As phosphor screen sample **15** was passed under X-ray slit **25**, the light that passed through optical slit **20** varied according to the profile of lateral light spread within phosphor screen sample **15**.

Any suitable source of X-radiation can be used for this test. To obtain the data described in this application, the X-radiation source was a commercially available Torrex 120D X-Ray Inspection System. Inside this system, the linear translation table that holds the entire assembly was under computer control (any suitable computer can be used). Integrating sphere **35** had a 4-inch (10.2 cm) diameter and was appropriately reflective. One such integrating sphere can be obtained from Labsphere. The top port of integrating sphere **35** that accepted the light from optical slit **20** was 1 inch (2.54 cm) in diameter. The side port that was used for PMT **30** was also 1 inch (2.54 cm) in diameter. While any suitable PMT can be used, we used a Hamamatsu 81925 with a quartz window for extended UV response. It was 1 inch (2.54 cm) in diameter, and had a very compact dynode chain so the length of the PMT was minimized. High voltage was supplied to PMT **30** by a 0-1kV power supply (not shown). A transimpedance amplifier (not shown) having a simple single RC bandwidth limitation of around 1 kHz was constructed. The signal from PMT **30** was low-pass filtered using a 24dB/octave active filter set at a bandwidth of 300 Hertz. A suitable computer system (for example, an Intel 486DX-33MHz DOS computer system) was used for data acquisition and analysis. The X-radiation source was slightly modified to allow for computer control and monitoring of the unit by the computer. Two digital output lines were used for START and STOP of the X-ray tube current, and one digital input line was used to monitor the XRAY ON signal to assure that the unit was indeed on.

LSP was measured in the following manner. The optical slit/integrating sphere/PMT assembly was moved relative to X-ray slit **25**. The X-radiation generation unit generated X-rays such that the intensity followed a 60 Hz single-wave rectified waveform in time as shown in FIG. 2. To take advantage of

this, a single data point that represents the value of the LSP at a given spatial position was generated by acquiring an array of data at each spatial position using time intervals between points in this temporal array small enough such that the X-ray intensity waveform can be adequately represented by this array of data.

- 5 Several repetitions of the waveform were captured in one array of data. A Fourier transform of this array of data yielded an array of data giving the amplitude of signal at various temporal frequencies that looked like that shown in FIG. 3. After the transform was done, the integral (sum) under the 60 and 120 Hz peaks was used as the value of the LSP at the current spatial position.

- 10 When the phosphor screen sample had been placed in the X-radiation generating unit, and the computer program for acquisition has been initiated, the program first set the proper high voltage to the PMT. This allows phosphor screens having varying brightness to be tested. After the computer had turned on the X-radiation generating unit, but prior to beginning the actual LSP data acquisition, the computer performed a brief data acquisition near the peak region of the LSP so that it can find the actual peak. The computer then positions the translation stage at this peak signal position and adjusted the PMT high voltage to provide peak signal between 1/2 and full scale of the analog-to-digital converter range. The translation stage was then moved 500 positions away from the peak and data acquisition is begun.

- 20 There are 1000 spatial positions, each separated by 10  $\mu$ m, at which the value of the LSP was determined. The peak of the LSP was approximated at data point 500. Given that the majority of the LSP data acquired represent baseline, for the first 400 values of the LSP and the last 400 values of the LSP, fewer actual data points were acquired, and the intermediate points (between the actual points) were determined by simple linear interpolation. For each actual data point in these "baseline" regions, the temporal data array was long enough to capture eight repetitions of the single wave rectified X-ray generator waveform. In an effort to minimize errors on the baseline from current bursts in the PMT, a running average value for the baseline was determined and the next data point must fall within some predetermined range of that running average or the
- 25
- 30

acquisition is repeated. For LSP data values 401-600, a data point was acquired at each spatial position. To improve the signal-to-noise in this portion of the LSP, effectively 32 repetitions of the waveform were captured (the average of 4 repeats of the 8 waveform acquisition). At the completion of the acquisition, the PMT high voltage was reduced to zero, the X-radiation generating unit was turned off, and the stage was positioned approximately at data point 500 (the peak of the LSP).

Substantial smoothing of the baseline of the data array was done to aid in subsequent analysis. A mirror analysis was done to assure symmetry to the LSP. This mirror analysis consists of varying the midpoint for the LSP array by amounts less than a full data point spacing, re-sampling the array by interpolation, then calculating the difference between points at mirror positions relative to a given midpoint. The value of the midpoint that gives the minimum difference between left and right is the optimal midpoint. The LSP array was then forced to be symmetric by placing the average value of two mirror points in place of the actual data value for each point in a mirror set. The value of the LSP at the peak position was determined by fitting a parabola to the two points on either side of, the peak position.

After this mirror analysis was completed, the baseline was subtracted. The baseline value removed was determined by averaging values at the beginning and the end of the data array. To eliminate noise in the resulting SSM caused by noise in the baseline data, the baseline data were replaced with an extrapolation of the LSP by fitting an exponential function (least squares method) to the LSP data from 4% down to 1% of the peak value. Then, a Hanning window was applied to the data:

$$(x'_n = x_n [0.5(1 - \cos(2\pi n / 1000))]).$$

Finally, the Fourier transform of the LSP was computed. The equation used for this transformation is

$$X_k = \frac{1}{N} \sum_{n=0}^{N-1} x_n e^{-2\pi i (\frac{nk}{N})}$$

wherein  $X_k$  represents the modulation at frequency  $k$ , and  $x_n$  is the measured LSP at spatial positions  $n$ . By the properties of the discrete Fourier Transform, the combination of 1000 data points at a spacing of 10  $\mu$  yielded an array of data after the Fourier Transform that are spaced every 0.1 cycles/mm. The modulation array was normalized to a value of 1.0 at zero spatial frequency. This modulation data gave a measure of the screen sharpness, i.e. the higher the modulation (closer to 1) at higher spatial frequencies, the sharper the image that the phosphor screen can produce. The value of the modulation at selected spatial frequencies is the "Screen Sharpness Measurement" (SSM).

Where two of the same screens ("symmetric screens") are used on opposing sides of the radiographic film in the imaging assemblies, the SSM value would be the same for each screen. Where two different screens ("asymmetric screens") are used on opposing sides of the radiographic film, the SSM value used in the practice of this invention is an average of the individual SSM values for the two screens.

For example, the fluorescent intensifying screens used in the practice of this invention are capable of providing an SSM value greater than those represented by reference Curve A of FIG. 4 at any point along Curve A over the spatial frequency range of from 0 to 10 cycles/mm. TABLE I below lists selected SSM vs. spatial frequency data from which FIG. 4 was generated. Preferred screens used in the practice of this invention are those having SSM values that are at least 1.1 times those represented by reference Curve A of FIG. 4 over a range a spatial frequency range of from 1 to 10 cycles/mm.

TABLE I

SSM	Spatial Frequency (cycles/mm)
1.000	0
0.821	0.5
0.547	1.0
0.357	1.5
0.240	2.0

0.165	2.5
0.118	3.0
0.087	3.5
0.066	4.0
0.053	4.5
0.044	5.0
0.038	5.5
0.032	6.0
0.028	6.5
0.024	7.0
0.020	7.5
0.017	8.0
0.015	8.5
0.013	9.0
0.011	9.5
0.010	10.0

The term “duplitized” is used to define a radiographic film having silver halide emulsion layers disposed on both the front- and backsides of the support. The radiographic silver halide films useful in the present invention are “duplitized.”

The radiographic silver halide films useful in the present invention are generally “symmetric” films wherein the sensitometric responses and properties are essentially the same on each side of the support. However, this does not necessarily mean that the silver halide emulsion layers on each side of the support are compositionally the same. In preferred embodiments, the films have essentially the same imaging and non-imaging layers on both sides of the support to give essentially the same sensitometric response and properties.

“Crossover” refers to radiation that images and passes through the emulsion layer(s) on one side of the support and images the emulsion layers on the

opposite side of the support. Measurements for crossover are determined by determining the density of the silver developed on a given side of the support. Densities can be determined using a standard densitometer. By plotting the density produced on each imaging side of the support versus the steps of a conventional step wedge (a measure of exposure), a characteristic sensitometric curve is generated for each imaging side of the material. At three different density levels in the relatively straight-line portions of the sensitometric curves between the toe and shoulder regions of the curves, the difference in speed ( $\Delta \log E$ ) between the two sensitometric curves is measured. The three density differences are then averaged and used in the following equation to calculate the % crossover:

$$\% \text{ Crossover} = \frac{1}{\text{antilog}(\Delta \log E) + 1} \times 100$$

In referring to grains and silver halide emulsions containing two or more halides, the halides are named in order of ascending molar concentrations.

The term "equivalent circular diameter" (ECD) is used to define the diameter of a circle having the same projected area as a silver halide grain. This can be measured using known techniques.

The term "aspect ratio" is used to define the ratio of grain ECD to grain thickness.

The term "coefficient of variation" (COV) is defined as 100 times the standard deviation (a) of grain ECD divided by the mean grain ECD.

The term "fluorescent intensifying screen" refers to a screen that absorbs X-radiation and emits light. A "prompt" emitting fluorescent intensifying screen will emit light immediately upon exposure to radiation while "storage" fluorescent screen can "store" the exposing X-radiation for emission at a later time when the screen is irradiated with other radiation (usually visible light).

The terms "front" (or frontside) and "back" (or backside) refer to layers, films, or fluorescent intensifying screens nearer to and farther from, respectively, the source of X-radiation.

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### **Radiographic Films**

The radiographic silver halide films useful in this invention have a speed of at least 700 and preferably of at least 800, and include a support having disposed on both sides thereof, two or more photographic silver halide  
10 emulsion layers and optionally one or more non-radiation sensitive hydrophilic layer(s). In preferred embodiments, "first" and "second" silver halide emulsion layers are disposed on the frontside of the support and "third" and "fourth" silver halide emulsion layers are disposed on the backside of the support, with the second and fourth silver halide emulsion layers being closer to the support  
15 (innermost silver halide emulsion layers) than the first and third silver halide emulsion layers (outermost silver halide emulsion layers).

In the more preferred embodiments, the two silver halide emulsion layers on each side of the support are essentially the same in chemical composition (for example, components, types of grains, silver halide  
20 composition, hydrophilic colloid binder composition, and g/m<sup>2</sup> coverage), and sensitometric properties but (as noted below) are different in thickness and hence silver and hydrophilic binder coverage. In such embodiments, the first and second silver halide emulsion layers are different in thickness and the third and fourth silver halide emulsion layers are different in thickness. More  
25 preferably, all of the silver halide emulsion layers have essentially the same chemical composition.

The support can take the form of any conventional radiographic support that is X-radiation and light transmissive. Useful supports for the films of this invention can be chosen from among those described in *Research Disclosure*,  
30 September 1996, Item 38957 (Section XV Supports) and *Research Disclosure*, Vol. 184, August 1979, Item 18431 (Section XII Film Supports). The support is

preferably a transparent flexible support. In its simplest possible form the transparent support consists of a transparent film chosen to allow direct adhesion of the hydrophilic silver halide emulsion layers or other hydrophilic layers. More commonly, the transparent support is itself hydrophobic and subbing layers are coated on the film to facilitate adhesion of the hydrophilic silver halide emulsion layers. Typically the support is either colorless or blue tinted (tinting dye being present in one or both of the support film and the subbing layers). Polyethylene terephthalate and polyethylene naphthalate are the preferred transparent support materials.

10                    In the more preferred embodiments, at least one non-light sensitive hydrophilic layer is included with the two or more silver halide emulsion layers on each side of the support. This layer may be an interlayer or overcoat, or both types of non-light sensitive layers can be present.

                    The first, second, third, and fourth silver halide emulsion layers  
15                    comprise predominantly (more than 50 %, and preferably at least 70%, of the total grain projected area) tabular silver halide grains. The grain composition can vary among the layers, but preferably, the grain composition is essentially the same in the first, second, third, and fourth silver halide emulsion layers. These tabular silver halide grains generally comprise at least 50, preferably at least 90, and more  
20                    preferably at least 95, mol % bromide, based on total silver in the emulsion layer. Such emulsions include silver halide grains composed of, for example, silver iodobromide, silver chlorobromide, silver iodochlorobromide, and silver chloriodobromide. The iodide grain content is generally up to 5 mol %, based on total silver in the emulsion layer. Preferably the iodide grain content is up to 3  
25                    mol %, and more preferably up to 1 mol % (based on total silver in the emulsion layer). Mixtures of different tabular silver halide grains can be used in any of the silver halide emulsion layers.

                    Any of the silver halide emulsion layers can also include some non-tabular silver halide grains having any desirable non-tabular morphology, or be  
30                    comprised of a mixture of two or more of such morphologies. The composition and methods of making such silver halide grains are well known in the art.

While the tabular silver halide grains can have any suitable aspect ratio, those used particularly in the first, second, third, and fourth silver halide emulsion layers generally and independently have an aspect ratio of 15 or more, preferably from 25 to 45, and more preferably, from 38 to 45.

5 In general, the tabular grains in any of the silver halide emulsion layers have an average grain diameter (ECD) of at least 3.0  $\mu\text{m}$ , and preferably of at least 3.5  $\mu\text{m}$ . The average grain diameters can be the same or different in the various emulsion layers. At least 100 non-overlapping tabular grains are measured to obtain the "average" ECD.

10 In addition, the tabular grains in the first, second, third, and fourth silver halide emulsion layers independently have an average thickness of from 0.06 to 0.16  $\mu\text{m}$ , and preferably from 0.08 to 0.14  $\mu\text{m}$ . Preferably, the average tabular grain thickness is essentially the same in all silver halide emulsion layers.

The procedures and equipment used to determine tabular grain size (and aspect ratio) are well known in the art. Tabular grain emulsions that have the desired composition and sizes are described in greater detail in the following patents:

U. S. Patents 4,414,310 (Dickerson), 4,425,425 (Abbott et al.), 4,425,426 (Abbott et al.), 4,439,520 (Kofron et al.), 4,434,226 (Wilgus et al.), 20 4,435,501 (Maskasky), 4,713,320 (Maskasky), 4,803,150 (Dickerson et al.), 4,900,355 (Dickerson et al.), 4,994,355 (Dickerson et al.), 4,997,750 (Dickerson et al.), 5,021,327 (Bunch et al.), 5,147,771 (Tsaur et al.), 5,147,772 (Tsaur et al.), 5,147,773 (Tsaur et al.), 5,171,659 (Tsaur et al.), 5,252,442 (Dickerson et al.), 5,370,977 (Zietlow), 5,391,469 (Dickerson), 5,399,470 (Dickerson et al.), 25 5,411,853 (Maskasky), 5,418,125 (Maskasky), 5,494,789 (Daubendiek et al.), 5,503,970 (Olm et al.), 5,536,632 (Wen et al.), 5,518,872 (King et al.), 5,567,580 (Fenton et al.), 5,573,902 (Daubendiek et al.), 5,576,156 (Dickerson), 5,576,168 (Daubendiek et al.), 5,576,171 (Olm et al.), and 5,582,965 (Deaton et al.).

The total dry unprocessed thickness and coating weight of the silver halide emulsion layers on opposing sides of the support can be the same or 30 different but preferably, they are the same. Where there are two silver halide

emulsion layers on each side of the support, they have different dry thickness wherein the outermost silver halide emulsion layers are thicker than the silver halide emulsion layers closer to the support. These evaluations are made on the dried film before it is contacted with processing solutions. Thus, the dry, unprocessed thickness ratio of the first silver halide emulsion layer to that of the second silver halide emulsion layer is greater than 1:1 (preferably from 3:1 to 1:1), and the dry, unprocessed thickness ratio of the third silver halide emulsion layer to that of the fourth silver halide emulsion layer is independently greater than 1:1 (preferably from 3:1 to 1:1). This generally means that the molar ratios of silver in the first to second, and third to fourth, silver halide emulsion layers, are independently greater than 1:1 (preferably from 1.5:1 to 3:1).

In addition, the silver halide emulsion layers closer to the support on both sides (that is the second and fourth silver halide emulsion layers) comprise one or more "crossover control agents" that are present in sufficient amounts to reduce light transmitted through the support to opposing layers to less than 15%, preferably less than 12%, and more preferably less than 10%. Crossover is measured in the practice of this invention as noted above.

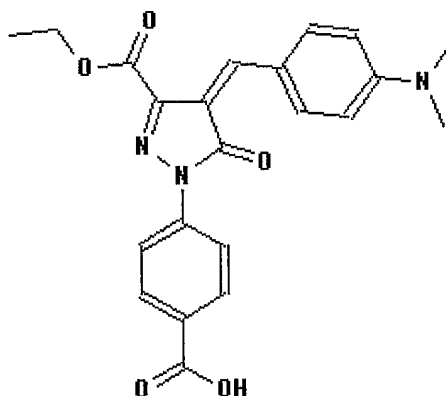
Useful crossover control agents are well known in the art and include one or more compounds that provide a total density of at least 0.3 (preferably at least 0.45) and up to 0.9 at a preferred wavelength of 545 nm and that are disposed on a transparent support. The density can be measured using a standard densitometer (using "visual status"). In general, the amount of crossover control agent in the "second" silver halide emulsion layer will vary depending upon the strength of absorption of the given compound(s), but for most pigments and dyes, the amount is generally from 0.75 to 1.5 mg/m<sup>2</sup> (preferably from 1 mg to 1.3 mg/m<sup>2</sup>).

In addition, the crossover control agents must be substantially removed within 90 seconds (preferably with 45 seconds) during processing (generally during development). By "substantially" means that the crossover control agent remaining in the film after processing provides no more than 0.05 optical density as measured using a conventional sensitometer. Removal of the

crossover control agents can be achieved by their migration out of the film, but preferably, they are not physically removed but are decolorized during processing.

Pigments and dyes that can be used as crossover control agents include various water-soluble, liquid crystalline, or particulate magenta or yellow filter dyes or pigments including those described for example in U.S. Patents 4,803,150 (Dickerson et al.), 5,213,956 (Diehl et al.), 5,399,690 (Diehl et al.), 5,922,523 (Helber et al.), and 6,214,499 (Helber et al.), and Japanese Kokai 2-123349, all of which are cited herein for pigments and dyes useful in the practice of this invention. One useful class of particulate dyes useful as crossover control agents includes nonionic polymethine dyes such as merocyanine, oxonol, hemioxonol, styryl, and arylidene dyes as described in U.S. Patent 4,803,150 (noted above) that is cited herein for the definitions of those dyes. The particulate magenta merocyanine and oxonol dyes are preferred and the magenta oxonol dyes are most preferred.

One particularly useful magenta oxonol dye that can be used as a crossover control agent is the following compound M-1:



M-1

A variety of silver halide dopants can be used, individually and in combination, in one or more of the silver halide emulsion layers to improve contrast as well as other common sensitometric properties. A summary of

conventional dopants is provided by *Research Disclosure*, Item 38957 [Section I Emulsion grains and their preparation, sub-section D) and grain modifying conditions and adjustments, paragraphs (3), (4), and (5)].

5 A general summary of silver halide emulsions and their preparation is provided in *Research Disclosure*, Item 38957 (Section I Emulsion grains and their preparation). After precipitation and before chemical sensitization the emulsions can be washed by any convenient conventional technique using techniques disclosed by *Research Disclosure*, Item 38957 (Section III Emulsion washing).

10 Any of the emulsions can be chemically sensitized by any convenient conventional technique as illustrated by *Research Disclosure*, Item 38957 (Section IV Chemical Sensitization). Sulfur, selenium or gold sensitization (or any combination thereof) is specifically contemplated. Sulfur sensitization is preferred, and can be carried out using for example, thiosulfates, thiosulfonates,  
15 thiocyanates, isothiocyanates, thioethers, thioureas, cysteine, or rhodanine. A combination of gold and sulfur sensitization is most preferred.

In addition, if desired, any of the silver halide emulsions can include one or more suitable spectral sensitizing dyes that include, for example, cyanine and merocyanine spectral sensitizing dyes. The useful amounts of such  
20 dyes are well known in the art but are generally within the range of from 200 to 1000 mg/mole of silver in the given emulsion layer. It is particularly preferred that all of the tabular silver halide grains used in the present invention (in all silver halide emulsion layers) be "green-sensitized", that is spectrally sensitized to radiation of from 470 to 570 nm of the electromagnetic spectrum. Various  
25 spectral sensitizing dyes are known for achieving this characteristic.

Instability that increases minimum density in negative-type emulsion coatings (that is fog) can be protected against by incorporation of stabilizers, antifoggants, antikinking agents, latent-image stabilizers and similar addenda in the emulsion and contiguous layers prior to coating. Such addenda are  
30

illustrated in *Research Disclosure*, Item 38957 (Section VII Antifoggants and stabilizers) and Item 18431 (Section II Emulsion Stabilizers, Antifoggants and Antikinking Agents).

It may also be desirable that one or more silver halide emulsion  
5 layers include one or more covering power enhancing compounds adsorbed to surfaces of the silver halide grains. A number of such materials are known in the art, but preferred covering power enhancing compounds contain at least one divalent sulfur atom that can take the form of a -S- or =S moiety. Such compounds are described in U.S. Patent 5,800,976 (Dickerson et al.) that is cited  
10 for the teaching of such sulfur-containing covering power enhancing compounds.

The silver halide emulsion layers and other hydrophilic layers on both sides of the support of the radiographic films generally contain conventional polymer vehicles (peptizers and binders) that include both synthetically prepared and naturally occurring colloids or polymers. The most preferred polymer  
15 vehicles include gelatin or gelatin derivatives alone or in combination with other vehicles. Conventional gelatino-vehicles and related layer features are disclosed in *Research Disclosure*, Item 38957 (Section II Vehicles, vehicle extenders, vehicle-like addenda and vehicle related addenda). The emulsions themselves can contain peptizers of the type set out in Section II, paragraph A. Gelatin and  
20 hydrophilic colloid peptizers. The hydrophilic colloid peptizers are also useful as binders and hence are commonly present in much higher concentrations than required to perform the peptizing function alone. The preferred gelatin vehicles include alkali-treated gelatin, acid-treated gelatin or gelatin derivatives (such as acetylated gelatin, deionized gelatin, oxidized gelatin and phthalated gelatin).  
25 Cationic starch used as a peptizer for tabular grains is described in U.S. Patents 5,620,840 (Maskasky) and 5,667,955 (Maskasky). Both hydrophobic and hydrophilic synthetic polymeric vehicles can be used also. Such materials include, but are not limited to, polyacrylates (including polymethacrylates), polystyrenes, polyacrylamides [including poly(methacrylamides)], and dextrans as described in  
30 U.S. Patent 5,876,913 (Dickerson et al.).

Thin, high aspect ratio tabular grain silver halide emulsions useful in the present invention will typically be prepared by processes including nucleation and subsequent growth steps. During nucleation, silver and halide salt solutions are combined to precipitate a population of silver halide nuclei in a reaction vessel. Double jet (addition of silver and halide salt solutions simultaneously) and single jet (addition of one salt solution, such as a silver salt solution, to a vessel already containing an excess of the other salt) process are known. During the subsequent growth step, silver and halide salt solutions, and/or preformed fine silver halide grains, are added to the nuclei in the reaction vessel, and the added silver and halide combines with the existing population of grain nuclei to form larger grains. Control of conditions for formation of high aspect ratio tabular grain silver bromide and iodobromide emulsions is known, for example, based upon U.S. Patents 4,434,226 (Wilgus et al.), 4,433,048 (Solberg et al.), and 4,439,520 (Kofron et al.). It is recognized, for example that the bromide ion concentration in solution at the stage of grain formation must be maintained within limits to achieve the desired tabularity of grains. As grain growth continues, the bromide ion concentration in solution becomes progressively less influential on the grain shape ultimately achieved. For example, U.S. Patent 4,434,226 (noted above) teaches the precipitation of high aspect ratio tabular grain silver bromoiodide emulsions at bromide ion concentrations in the pBr range of from 0.6 to 1.6 during grain nucleation, with the pBr range being expanded to 0.6 to 2.2 during subsequent grain growth. U.S. Patent 4,439,520 (noted above) extends these teachings to the precipitation of high aspect ratio tabular grain silver bromide emulsions. pBr is defined as the negative log of the solution bromide ion concentration. U.S. Patent 4,414,310 (Daubendiek et al.) describes a process for the preparation of high aspect ratio silver bromoiodide emulsions under pBr conditions not exceeding the value of 1.64 during grain nucleation. U.S. Patent 4,713,320 (Maskasky), in the preparation of high aspect ratio silver halide emulsions, teaches that the useful pBr range during nucleation can be extended to a value of 2.4 when the precipitation of the tabular silver bromide or bromoiodide grains occurs in the presence of gelatino-peptizer containing less than 30

micromoles of methionine (for example oxidized gelatin) per gram. The use of such oxidized gel also enables the preparation of thinner and/or larger diameter grains, and/or more uniform grain populations containing fewer non-tabular grains.

5                   The use of oxidized gelatin as peptizer during nucleation, such as taught by U.S. Patent 4,713,320 (noted above), is particularly preferred for making thin, high aspect ratio tabular grain emulsions for use in the present invention, employing either double or single jet nucleation processes. As gelatin employed as peptizer during nucleation typically will comprise only a fraction of the total  
10   gelatin employed in an emulsion, the percentage of oxidized gelatin in the resulting emulsion may be relatively small, that is, at least 0.05% (based on total dry weight of hydrophilic polymer vehicle mixture). However, more gelatin (including oxidized gelatin) is usually added to the formulation at later stages (for example, growth stage) so that the total oxidized gelatin can be greater, and for  
15   practical purposes as high as 18% (based on total dry weight of hydrophilic polymer vehicle mixture in the silver halide emulsion layer).

                  Thus it is preferred that the coated first, second, third, and fourth tabular grain silver halide emulsion layers comprise tabular silver halide grains dispersed in a hydrophilic polymeric vehicle mixture comprising at least 0.05%,  
20   preferably at least 1%, and more preferably at least 5%, of oxidized gelatin based on the total dry weight of hydrophilic polymer vehicle mixture in that coated silver halide emulsion layer. The upper limit for the oxidized gelatin is not critical but for practical purposes, it is 18% and preferably up to 15%, based on the total dry weight of the hydrophilic polymer vehicle mixture. Preferably, from 5 to 15% (by  
25   dry weight) of the hydrophilic polymer vehicle mixture is oxidized gelatin. The amount of oxidized gelatin in the emulsion layers can be the same or different. Preferably, it is the same amount in all silver halide emulsion layers.

                  The oxidized gelatin may be in the form of deionized oxidized gelatin but non-deionized oxidized gelatin may be preferred because of the  
30   presence of ions, or a mixture of deionized and non-deionized oxidized gelatins can be used. Deionized or non-deionized oxidized gelatin generally has the

property of relatively lower amounts of methionine per gram of gelatin than other forms of gelatin. Preferably, the amount of methionine is from 0 to 3  $\mu\text{mol}$  of methionine, and more preferably from 0 to 1  $\mu\text{mol}$  of methionine, per gram of gelatin. This material can be prepared using known procedures.

5                   The remainder of the polymeric vehicle mixture can be any of the hydrophilic vehicles described above, but preferably it is composed of alkali-treated gelatin, acid-treated gelatin acetylated gelatin, or phthalated gelatin.

                  The silver halide emulsions containing the tabular silver halide grains described above can be prepared as noted using a considerable amount of oxidized gelatin (preferably deionized oxidized gelatin) during grain nucleation and growth, and then additional polymeric binder can be added to provide the coating formulation. The amounts of oxidized gelatin in the emulsion can be as low as 0.3 g/mol of silver and as high as 27 g/mol of silver in the emulsion. Preferably, the amount of oxidized gelatin in the emulsion is from 1 to 20 g/mol of silver.

10                   The silver halide emulsion layers (and other hydrophilic layers) in the radiographic films are generally fully hardened using one or more conventional hardeners. Thus, the amount of hardener on each side of the support can be the same or different and is generally at least 1% and preferably at least 1.5%, based on the total dry weight of the polymer vehicles on each side of the support.

15                   The levels of silver and polymer vehicle in the radiographic silver halide film can vary in the various silver halide emulsion layers. In general, the total amount of silver on each side of the support is at least 10 and no more than 25  $\text{mg}/\text{dm}^2$  (preferably from 18 to 24  $\text{mg}/\text{dm}^2$ ). In addition, the total coverage of polymer vehicle on each side of the support is generally at least 20 and no more than 40  $\text{mg}/\text{dm}^2$  (preferably from 30 to 40  $\text{mg}/\text{dm}^2$ ). The amounts of silver and polymer vehicle on the two sides of the support in the radiographic silver halide film can be the same or different as long as the sensitometric properties on both sides are the same. These amounts refer to dry weights.

20                   The silver halide emulsion layers (and other hydrophilic layers) in the radiographic films are generally fully hardened using one or more conventional hardeners. Thus, the amount of hardener on each side of the support can be the same or different and is generally at least 1% and preferably at least 1.5%, based on the total dry weight of the polymer vehicles on each side of the support.

25                   The levels of silver and polymer vehicle in the radiographic silver halide film can vary in the various silver halide emulsion layers. In general, the total amount of silver on each side of the support is at least 10 and no more than 25  $\text{mg}/\text{dm}^2$  (preferably from 18 to 24  $\text{mg}/\text{dm}^2$ ). In addition, the total coverage of polymer vehicle on each side of the support is generally at least 20 and no more than 40  $\text{mg}/\text{dm}^2$  (preferably from 30 to 40  $\text{mg}/\text{dm}^2$ ). The amounts of silver and polymer vehicle on the two sides of the support in the radiographic silver halide film can be the same or different as long as the sensitometric properties on both sides are the same. These amounts refer to dry weights.

30                   The levels of silver and polymer vehicle in the radiographic silver halide film can vary in the various silver halide emulsion layers. In general, the total amount of silver on each side of the support is at least 10 and no more than 25  $\text{mg}/\text{dm}^2$  (preferably from 18 to 24  $\text{mg}/\text{dm}^2$ ). In addition, the total coverage of polymer vehicle on each side of the support is generally at least 20 and no more than 40  $\text{mg}/\text{dm}^2$  (preferably from 30 to 40  $\text{mg}/\text{dm}^2$ ). The amounts of silver and polymer vehicle on the two sides of the support in the radiographic silver halide film can be the same or different as long as the sensitometric properties on both sides are the same. These amounts refer to dry weights.

In addition, the molar ratio of silver in the first silver halide emulsion layer to that of the second silver halide emulsion layer is greater than 1:1 (preferably from 1.5:1 to 3:1), and the molar ratio of silver in the third silver halide emulsion layer to that of the fourth silver halide emulsion layer is independently greater than 1:1 (preferably from 1.5:1 to 3:1).

The radiographic silver halide films generally include a surface protective overcoat disposed on each side of the support that typically provides for physical protection of the various layers underneath. Each protective overcoat can be sub-divided into two or more individual layers. For example, protective overcoats can be sub-divided into surface overcoats and interlayers (between the overcoat and silver halide emulsion layers). In addition to vehicle features discussed above the protective overcoats can contain various addenda to modify the physical properties of the overcoats. Such addenda are described in *Research Disclosure*, Item 38957 (Section IX Coating physical property modifying addenda, A. Coating aids, B. Plasticizers and lubricants, C. Antistats, and D. Matting agents). Interlayers that are typically thin hydrophilic colloid layers can be used to provide a separation between the silver halide emulsion layers and the surface overcoats or between the silver halide emulsion layers. The overcoat on at least one side of the support can also include a blue toning dye or a tetraazaindene (such as 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene) if desired.

The protective overcoat is generally comprised of one or more hydrophilic colloid vehicles, chosen from among the same types disclosed above in connection with the emulsion layers.

The various coated layers of radiographic silver halide films can also contain tinting dyes to modify the image tone to transmitted or reflected light. These dyes are not decolorized during processing and may be homogeneously or heterogeneously dispersed in the various layers. Preferably, such non-bleachable tinting dyes are in a silver halide emulsion layer.

### Imaging Assemblies

The radiographic imaging assemblies are composed of one radiographic silver halide film as described herein and two fluorescent intensifying screens to provide a cumulative system speed of at least 800 (preferably at least 1100) for the entire imaging "system". The film and screens are generally arranged in a suitable "cassette" designed for this purpose. One screen is on the "frontside" (first exposed to X-radiation) and the other on the "backside" of the film. They can be the same or different in phosphor, phosphor coverage, speed, or other properties. Fluorescent intensifying screens are typically designed to absorb X-rays and to emit electromagnetic radiation having a wavelength greater than 300 nm. These screens can take any convenient form providing they meet all of the usual requirements for use in radiographic imaging. Examples of conventional, useful fluorescent intensifying screens are provided by *Research Disclosure*, Item 18431 (Section IX X-Ray Screens/Phosphors) and U.S. Patents 5,021,327 (Bunch et al.), 4,994,355 (Dickerson et al.), 4,997,750 (Dickerson et al.), and 5,108,881 (Dickerson et al.). The fluorescent layer contains phosphor particles and a binder, and may also contain a light scattering material, such as titania.

Any conventional or useful phosphor can be used, singly or in mixtures, in the intensifying screens used in the practice of this invention. For example, useful phosphors are described in numerous references relating to fluorescent intensifying screens including *Research Disclosure*, Vol. 184, August 1979, Item 18431 (Section IX X-ray Screens/Phosphors) and U.S. Patents 2,303,942 (Wynd et al.), 3,778,615 (Luckey), 4,032,471 (Luckey), 4,225,653 (Brixner et al.), 3,418,246 (Royce), 3,428,247 (Yocon), 3,725,704 (Buchanan et al.), 2,725,704 (Swindells), 3,617,743 (Rabatin), 3,974,389 (Ferri et al.), 3,591,516 (Rabatin), 3,607,770 (Rabatin), 3,666,676 (Rabatin), 3,795,814 (Rabatin), 4,405,691 (Yale), 4,311,487 (Luckey et al.), 4,387,141 (Patten), 4,021,327 (Bunch et al.), 4,865,944 (Roberts et al.), 4,994,355 (Dickerson et al.), 4,997,750 (Dickerson et al.), 5,064,729 (Zegarski), 5,108,881 (Dickerson et al.),

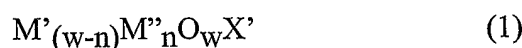
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5,250,366 (Nakajima et al.), and 5,871,892 (Dickerson et al.), and EP 0 491,116A1 (Benzo et al.), the disclosures of all of which are cited with respect to the phosphors.

The inorganic phosphor can be calcium tungstate, activated or unactivated lithium stannates, niobium and/or rare earth activated or unactivated yttrium, lutetium, or gadolinium tantalates, rare earth-activated or unactivated middle chalcogen phosphors such as rare earth oxychalcogenides and oxyhalides, or terbium-activated or unactivated lanthanum or lutetium middle chalcogen phosphor, or the inorganic phosphor can contain hafnium.

Still other useful phosphors are those containing hafnium as described for example in U.S. Patents 4,988,880 (Bryan et al.), 4,988,881 (Bryan et al.), 4,994,205 (Bryan et al.), 5,095,218 (Bryan et al.), 5,112,700 (Lambert et al.), 5,124,072 (Dole et al.), and 5,336,893 (Smith et al.).

Alternatively, the inorganic phosphor is a rare earth oxychalcogenide and oxyhalide phosphor that is represented by the following formula (1):



wherein M' is at least one of the metals yttrium (Y), lanthanum (La), gadolinium (Gd), or lutetium (Lu), M'' is at least one of the rare earth metals, preferably dysprosium (Dy), erbium (Er), europium (Eu), holmium (Ho), neodymium (Nd), praseodymium (Pr), samarium (Sm), tantalum (Ta), terbium (Tb), thulium (Tm), or ytterbium (Yb), X' is a middle chalcogen (S, Se, or Te) or halogen, n is 0.002 to 0.2, and w is 1 when X' is halogen or 2 when X' is a middle chalcogen.

Particularly preferred phosphors of formula (1) include a lanthanum oxybromides, or terbium-activated or thulium-activated gadolinium oxides or oxysulfides (such as  $Gd_2O_2S:Tb$ ).

Other suitable phosphors are described in U.S. Patents 4,835,397 (Arakawa et al.) and 5,381,015 (Dooms), and include for example divalent europium and other rare earth activated alkaline earth metal halide phosphors and rare earth element activated rare earth oxyhalide phosphors. Of these types of

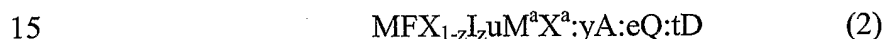
phosphors, the more preferred phosphors include alkaline earth metal fluorohalide prompt emitting and/or storage phosphors [particularly those containing iodide such as alkaline earth metal fluorobromiodide storage phosphors as described in U.S. Patent 5,464,568 (Bringley et al.)].

5 Another class of useful phosphors includes rare earth hosts such as rare earth activated mixed alkaline earth metal sulfates such as europium-activated barium strontium sulfate.

Particularly useful phosphors are those containing doped or undoped tantalum such as  $\text{YTaO}_4$ ,  $\text{YTaO}_4\text{:Nb}$ ,  $\text{Y(Sr)TaO}_4$ , and  $\text{Y(Sr)TaO}_4\text{:Nb}$ .

10 These phosphors are described in U.S. Patents 4,226,653 (Brixner), 5,064,729 (Zegarski), 5,250,366 (Nakajima et al.), and 5,626,957 (Benso et al.).

In other embodiments, the inorganic phosphor is an alkaline earth metal phosphor that is the product of firing starting materials comprising optional oxide and a combination of species characterized by the following formula (2):



wherein "M" is magnesium (Mg), calcium (Ca), strontium (Sr), or barium (Ba), "F" is fluoride, "X" is chloride (Cl) or bromide (Br), "I" is iodide,  $\text{M}^a$  is sodium (Na), potassium (K), rubidium (Rb), or cesium (Cs),  $\text{X}^a$  is fluoride (F), chloride (Cl), bromide (Br), or iodide (I), "A" is europium (Eu), cerium (Ce), samarium (Sm), or terbium (Tb), "Q" is  $\text{BeO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{SrO}$ ,  $\text{BaO}$ ,  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{GeO}_2$ ,  $\text{SnO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$ , or  $\text{ThO}_2$ , "D" is vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), or nickel (Ni), "z" is 0 to 1, "u" is from 0 to 1, "y" is from  $1 \times 10^{-4}$  to 0.1, "e" is from 0 to 1, and "t" is from 0 to 0.01. These definitions apply wherever they are found in this application unless specifically stated to the contrary. It is also contemplated that "M", "X", "A", and "D" represent multiple elements in the groups identified above.

25

The phosphor can be dispersed in a suitable binder(s) in a phosphor layer. A particularly useful binder is a polyurethane binder such as that commercially available under the trademark Permuthane.

30

The fluorescent intensifying screens useful in this invention exhibit a photographic speed of at least 600. One preferred phosphor is a terbium activated gadolinium oxysulfide. A skilled worker in the art would be able to choose the appropriate inorganic phosphor, its particle size, and coverage in the phosphor layer to provide the desired screen speed. In preferred embodiments, the coverage of the inorganic phosphor in the phosphor layer is from 4 to 15 g/dm<sup>2</sup> at a phosphor to binder weight ratio of from 18:1 to 20:1. A particularly useful fluorescent intensifying screen of containing this phosphor layer is Kodak Lanex<sup>®</sup> Fast that is available from Eastman Kodak Company and is described in general as Screen Y in the Example 1 below. This screen can be prepared using components and procedures known by one skilled in the art.

Support materials for radiographic screens in accordance with the present invention include cardboard, plastic films such as films of cellulose acetate, polyvinyl chloride, polyvinyl acetate, polyacrylonitrile, polystyrene, polyester, polyethylene terephthalate, polyamide, polyimide, cellulose triacetate and polycarbonate, metal sheets such as aluminum foil and aluminum alloy foil, ordinary papers, baryta paper, resin-coated papers, pigmented papers containing titanium dioxide or the like, and papers sized with polyvinyl alcohol or the like. A flexible plastic film is preferably used as the support material.

The plastic film may contain a light-absorbing material such as carbon black, or may contain a light-reflecting material such as titanium dioxide or barium sulfate. The former is appropriate for preparing a high-resolution type radiographic screen, while the latter is appropriate for preparing a high-sensitivity type radiographic screen. For use in this invention it is highly preferred that the support absorb substantially all of the radiation emitted by the phosphor. Examples of particularly preferred supports include polyethylene terephthalate, blue colored or black colored (for example, LUMIRROR C, type X30 supplied by Toray Industries, Tokyo, Japan). These supports may have a thickness that may differ depending on the material of the support, and may generally be between 60 and 1000  $\mu\text{m}$ , more preferably between 80 and 500  $\mu\text{m}$  from the standpoint of handling.

In preferred embodiments of this invention, flexible support materials for the screens include a specific reflective substrate that is a single- or multi-layer reflective sheet. At least one of the layers of this sheet is a reflective substrate that comprises a continuous polymer (particularly a polyester) first phase and a second phase dispersed within the continuous polymer first phase. This second phase comprises microvoids containing suitable reflective inorganic particles (especially barium sulfate particles).

Such a support is capable of reflecting at least 90% (preferably at least 94%) of incident radiation having a wavelength of from 300 to 700 nm. This property is achieved by the judicious selection of the polymer first phase, microvoids and proportion thereof, amount of inorganic particles such as barium sulfate particles, and the use of multiple layers having microvoids and/or particles.

The continuous polymer first phase of the reflective substrate provides a matrix for the other components of the reflective substrate and is transparent to longer wavelength electromagnetic radiation. This polymer phase can comprise a film or sheet of one or more thermoplastic polyesters, which film has been biaxially stretched (that is, stretched in both the longitudinal and transverse directions) to create the microvoids therein around the inorganic particles. Any suitable polyester can be used as long as it can be cast, spun, molded, or otherwise formed into a film or sheet, and can be biaxially oriented as noted above. Generally, the polyesters have a glass transition temperature of from 50 to 150°C (preferably from 60 to 100°C) as determined using a differential scanning calorimeter (DSC).

Suitable polyesters that can be used include, but are not limited to, poly(1,4-cyclohexylene dimethylene terephthalate), poly(ethylene terephthalate), poly(ethylene naphthalate), and poly(1,3-cyclohexylene dimethylene terephthalate). Poly(1,4-cyclohexylene dimethylene terephthalate) is most preferred.

The ratio of the reflective index of the continuous polymer first phase to the second phase is from 1.4:1 to 1.6:1.

As noted above, it is preferred that barium sulfate particles are incorporated into the continuous polyester phase as described below. These particles generally have an average particle size of from 0.6 to 2  $\mu\text{m}$  (preferably from 0.7 to 1.0  $\mu\text{m}$ ). In addition, these particles comprise from 35 to 65 weight %  
5 (preferably from 55 to 60 weight %) of the total dry reflective substrate weight, and from 15 to 25% of the total reflective substrate volume.

The barium sulfate particles can be incorporated into the continuous polyester phase by various means. For example, they can be incorporated during polymerization of the dicarboxylic acid(s) and polyol(s) used  
10 to make the continuous polyester first phase. Alternatively and preferably, they are incorporated by mixing them into pellets of the polyester and extruding the mixture to produce a melt stream that is cooled into the desired sheet containing barium sulfate particles dispersed therein.

These particles are at least partially bordered by voids because they  
15 are embedded in the microvoids distributed throughout the continuous polymer first phase. Thus, the microvoids containing the particles comprise a second phase dispersed within the continuous polymer first phase. The microvoids generally occupy from 35 to 60% (by volume) of the dry reflective substrate.

The microvoids can be of any particular shape, that is circular,  
20 elliptical, convex, or any other shape reflecting the film orientation process and the shape and size of the barium sulfate particles. The size and ultimate physical properties of the microvoids depend upon the degree and balance of the orientation, temperature and rate of stretching, crystallization characteristics of the polymer, the size and distribution of the particles, and other considerations that  
25 would be apparent to one skilled in the art. Generally, the microvoids are formed when the extruded sheet containing particles is biaxially stretched using conventional orientation techniques.

Thus, in general, the reflective substrates used in the practice of this invention are prepared by:

- 30 (a) blending the inorganic particles (such as barium sulfate particles) into a desired polymer (such as a polyester) as the continuous phase,

(b) forming a sheet of the polymer containing the particles, such as by extrusion, and

(c) stretching the sheet in one or transverse directions to form microvoids around the particles.

5           The present invention does not require but permits the use or addition of various organic and inorganic materials such as pigments, anti-block agents, antistatic agents, plasticizers, dyes, stabilizers, nucleating agents, and other addenda known in the art to the reflective substrate. These materials may be incorporated into the polymer phase or they may exist as separate dispersed phases  
10 and can be incorporated into the polymer using known techniques.

          The reflective substrate can have a thickness (dry) of from 100 to 400  $\mu\text{m}$  (preferably from 150 to 225  $\mu\text{m}$ ). If there are multiple reflective substrates in the support, their thickness can be the same or different.

          As noted above, the reflective substrate can be the sole layer of the  
15 support for the phosphor screen, but in some preferred embodiments, additional layers are formed or laminated with one or more reflective substrate to form a multi-layer or multi-strata support. In preferred embodiments, the support further comprises an additional layer such as a stretch microvoided polyester layer that has similar composition as the reflective substrate except that barium sulfate  
20 particles are omitted. This additional polyester layer is arranged adjacent the reflective substrate, but opposite the phosphor layer. In other words, the reflective layer is closer to the phosphor layer than the microvoided polyester layer.

          The microvoided polymer layers can comprise microvoids in an amount of from 35 to 60% (by total layer volume). The additional layers (with or  
25 without microvoids) can have a dry thickness of from 30 to 120  $\mu\text{m}$  (preferably from 50 to 70  $\mu\text{m}$ ). The polymer(s) in the additional layer can be same or different as those in the reflective substrate.

          These additional microvoided polymer layers can also include organic or inorganic particles in the microvoids as long as those particles are not  
30 same particles as in the primary reflective layer. Useful particles includes polymeric beads (such as cellulose acetate particles), crosslinked polymeric

microbeads, immiscible polymer particles (such as polypropylene particles), and other particulate materials known in the art that will not interfere with the desired reflectivity of the support required for the present invention.

Another representative fluorescent intensifying screen useful in the present invention is described as Screen V in Example 2 below.

### Imaging and Processing

Exposure and processing of the radiographic silver halide films can be undertaken in any convenient conventional manner. The exposure and processing techniques of U.S. Patents 5,021,327 and 5,576,156 (both noted above) are typical for processing radiographic films. Exposing X-radiation is generally directed through a patient and through a fluorescent intensifying screen arranged against the frontside of the film before it passes through the radiographic silver halide film, and the second fluorescent intensifying screen.

Processing compositions (both developing and fixing compositions) are described in U.S. Patents 5,738,979 (Fitterman et al.), 5,866,309 (Fitterman et al.), 5,871,890 (Fitterman et al.), 5,935,770 (Fitterman et al.), and 5,942,378 (Fitterman et al.). The processing compositions can be supplied as single- or multi-part formulations, and in concentrated form or as more diluted working strength solutions.

It is particularly desirable that the radiographic silver halide films be processed within 90 seconds ("dry-to-dry") and preferably at least 20 seconds and up to 60 seconds, including the developing, fixing and any washing (or rinsing) steps, before drying. Such processing can be carried out in any suitable processing equipment including but not limited to, a Kodak X-OMAT<sup>®</sup> RA 480 processor that can utilize Kodak Rapid Access processing chemistry. Other "rapid access processors" are described for example in U.S. Patent 3,545,971 (Barnes et al.) and EP 0 248,390A1 (Akio et al.). Preferably, the black-and-white developing compositions used during processing are free of any photographic film hardeners, such as glutaraldehyde.

Radiographic kits can include an imaging assembly, additional fluorescent intensifying screens and/or metal screens, additional radiographic silver halide films, and/or one or more suitable processing compositions (for example black-and-white developing and fixing compositions).

5                   The following example is presented for illustration and the invention is not to be interpreted as limited thereby.

**Example 1:**

Radiographic Film A:

10                   Radiographic Film A was a duplitized film having the same silver halide emulsion on each side of a blue-tinted 170  $\mu\text{m}$  transparent poly(ethylene terephthalate) film support and an interlayer and overcoat layer over each emulsion layer. The emulsions of Film A were not prepared using oxidized gelatin.

15                   Radiographic Film A had the following layer arrangement:  
Overcoat  
Interlayer  
Emulsion Layer  
Support  
Emulsion Layer  
20                   Interlayer  
Overcoat

The noted layers were prepared from the following formulations.

25	<u>Overcoat Formulation</u>	<u>Coverage (mg/dm<sup>2</sup>)</u>
	Gelatin vehicle	3.4
	Methyl methacrylate matte beads	0.14
	Carboxymethyl casein	0.57
	Colloidal silica (LUDOX AM)	0.57
30	Polyacrylamide	0.57
	Chrome alum	0.025
	Resorcinol	0.058
	Spermafol	0.15

	<u>Interlayer Formulation</u>	<u>Coverage (mg/dm<sup>2</sup>)</u>
	Gelatin vehicle	3.4
	Carboxymethyl casein	0.57
5	Colloidal silica (LUDOX AM)	0.57
	Polyacrylamide	0.57
	Chrome alum	0.025
	Resorcinol	0.058
	Nitron	0.044
10	<u>Emulsion Layer Formulation</u>	<u>Coverage (mg/dm<sup>2</sup>)</u>
	Tabular grains	
	[AgBr 2.9 $\mu$ m ave. dia. x 0.10 $\mu$ m thickness]	16.1 Ag
	Gelatin vehicle	26.3
15	4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene	2.1 g/Ag mole
	Potassium nitrate	1.8
	Maleic acid hydrazide	0.0087
	Sorbitol	0.53
	Glycerin	0.57
20	Potassium bromide	0.14
	Resorcinol	0.44
	Bisvinylsulfonylmethane	2% based on total gelatin in all layers on same side
25		

Radiographic Film B:

Radiographic Film B was like Radiographic Film A except that larger tabular silver halide grains having an average diameter of 2.9  $\mu$ m and thickness of 0.12  $\mu$ m were used in the emulsion layers. These tabular silver halide grains were coated in each emulsion layer at 18.3 mg/dm<sup>2</sup>.

Radiographic Film C:

Radiographic Film C was duplitized, symmetric radiographic film with two different silver halide emulsion layers on each side of the support. The two emulsion layers contained tabular silver halide grains that were prepared and dispersed in oxidized gelatin that had been added at multiple times before and/or during the nucleation and early growth of the silver bromide tabular grains dispersed therein. The tabular grains in each silver halide emulsion layer had a mean aspect ratio of about 44. The nucleation and early growth of the tabular grains were performed using a "bromide-ion-concentration free-fall" process in which a dilute silver nitrate solution was slowly added to a bromide ion-rich deionized oxidized gelatin environment. The grains were chemically sensitized with sulfur, gold, and selenium using conventional procedures. Spectral sensitization to about 560 nm was provided using anhydro-5,5-dichloro-9-ethyl-3,3'-bis(3-sulfopropyl)oxacarbocyanine hydroxide (680 mg/mole of silver) followed by potassium iodide (400 mg/mole of silver).

Radiographic Film C had the following layer arrangement and formulations on the film support:

	Overcoat
	Interlayer
20	Emulsion Layer 1
	Emulsion Layer 2
	Support
	Emulsion Layer 2
	Emulsion Layer 1
25	Interlayer
	Overcoat

	<u>Overcoat Formulation</u>	<u>Coverage (mg/dm<sup>2</sup>)</u>
	Gelatin vehicle	3.4
30	Methyl methacrylate matte beads	0.14
	Carboxymethyl casein	0.57

	Colloidal silica (LUDOX AM)	0.57
	Polyacrylamide	0.57
	Chrome alum	0.025
	Resorcinol	0.058
5	Spermafol	0.15
	<u>Interlayer Formulation</u>	<u>Coverage (mg/dm<sup>2</sup>)</u>
	Gelatin vehicle	3.4
	Carboxymethyl casein	0.57
10	Colloidal silica (LUDOX AM)	0.57
	Polyacrylamide	0.57
	Chrome alum	0.025
	Resorcinol	0.058
	Nitron	0.044
15	<u>Emulsion Layer 1 Formulation</u>	<u>Coverage (mg/dm<sup>2</sup>)</u>
	Tabular grains	
	[AgBr 4.4 $\mu$ m ave. dia. x 0.10 $\mu$ m thickness]	12.9 Ag
	Oxidized gelatin vehicle	2.2
20	Non-oxidized gelatin vehicle	15
	4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene	2.1 g/Ag mole
	Potassium nitrate	1.8
	Ammonium hexachloropalladate	0.0022
25	Maleic acid hydrazide	0.0087
	Sorbitol	0.53
	Glycerin	0.57
	Potassium bromide	0.14
	Resorcinol	0.44
30		

	<u>Emulsion Layer 2 Formulation</u>	<u>Coverage (mg/dm<sup>2</sup>)</u>
	Tabular grains	
	[AgBr 4.4 $\mu\text{m}$ ave. dia. x 0.10 $\mu\text{m}$ thickness]	6.5 Ag
	Oxidized gelatin vehicle	1.1
5	Non-oxidized gelatin vehicle	7.5
	Microcrystalline Dye M-1 (shown above)	1.08
	5-Bromo-4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene	0.7 g/Ag mole
	Potassium nitrate	1.1
10	Ammonium hexachloropalladate	0.013
	Maleic acid hydrazide	0.0053
	Sorbitol	0.32
	Glycerin	0.35
	Potassium bromide	0.083
15	Resorcinol	0.26
	Bisvinylsulfonylmethane	2% based on total gelatin on same side

20 The cassettes used for imaging contained a pair of the following screens on opposing sides of the noted radiographic films:

25 Fluorescent intensifying screen "X" was prepared using known procedures and components to have a terbium activated gadolinium oxysulfide phosphor (median particle size of 7.8 to 8  $\mu\text{m}$ ) dispersed in a Permuthane<sup>TM</sup> polyurethane binder on a white-pigmented poly(ethylene terephthalate) film support. The total phosphor coverage was 4.83 g/dm<sup>2</sup> and the phosphor to binder weight ratio was 19:1. The screen speed was 440.

30 Fluorescent intensifying screens "Y" were prepared using known procedures and components and included two different ("asymmetric") screens, one for the frontside of the film and the other for the backside. Each screen comprised a terbium activated gadolinium oxysulfide phosphor layer on a white-

pigmented poly(ethylene terephthalate) film support. The phosphor (median particle size of 7.8 to 8  $\mu\text{m}$ ) was dispersed in a Permuthane<sup>TM</sup> polyurethane binder. The total phosphor coverage in the screen used on the frontside ("exposed side") was 4.83  $\text{g}/\text{dm}^2$  and the total phosphor coverage on the screen used on the backside was 13.5  $\text{g}/\text{dm}^2$ . The phosphor to binder weight ratio in each screen was 19:1. The screen speed was 600.

Samples of the films in the imaging assemblies were exposed using an inverse square X-ray sensitometer (device that makes exceedingly reproducible X-ray exposures). A lead screw moved the detector between exposures. By use of the inverse square law, distances were selected that produced exposures that differed by 0.1 logE. The length of the exposures was constant. This instrument provided sensitometry that gives the response of the detector to an imagewise exposure where all of the image is exposed for the same length of time, but the intensity is changed due to the anatomy transmitting more or less of the X-radiation flux.

The exposed film samples were processed using a commercially available KODAK RP X-OMAT<sup>®</sup> Film Processor M6A-N, M6B, or M35A. Development was carried out using the following black-and-white developing composition:

20	Hydroquinone	30 g
	Phenidone	1.5 g
	Potassium hydroxide	21 g
	$\text{NaHCO}_3$	7.5 g
25	$\text{K}_2\text{SO}_3$	44.2 g
	$\text{Na}_2\text{S}_2\text{O}_5$	12.6 g
	Sodium bromide	35 g
	5-Methylbenzotriazole	0.06 g
	Glutaraldehyde	4.9 g
30	Water to 1 liter, pH 10	

Fixing was carried out using KODAK RP X-OMAT<sup>®</sup> LO Fixer and Replenisher fixing composition (Eastman Kodak Company). The film samples were processed in each instance for less than 90 seconds (dry-to-dry).

Optical densities are expressed below in terms of diffuse density as measured by a conventional X-rite<sup>™</sup> Model 310 densitometer that was calibrated to ANSI standard PH 2.19 and was traceable to a National Bureau of Standards calibration step tablet. The characteristic density vs. logE curve was plotted for each radiographic film that was exposed and processed as noted above. Photographic speed was measured at a density of  $1.0 + D_{\min}$ . TABLE II below shows a change in system speed of the imaging assemblies. "SSM" data for the screens were determined as described above. Only the SSM values at 2 cycles/mm are reported in TABLE II but FIG. 4 shows the SSM data over the entire range of spatial frequencies for Screen Y (average SSM values for the two asymmetric screens) in an imaging assembly of the present invention. The % crossover was measured using a procedure like that described above.

The following TABLE II shows the sensitometric data of Radiographic Films A-C when exposed with various screens. The data show that system speed can be increased by using a higher speed film and even further increased by using the higher speed Screen Y compared to Screen X with those films. However, this increase in system speed resulted in reduced SSM values when Screen Y was used.

Moreover, the combination of Film C with Screen X provided higher system speed with higher SSM values than the combinations of either Film A or B with Screen X or Y. In addition, the combination of Film C with Screen Y provided even greater system speed with an SSM value comparable to the "slowest" film/screen combinations. Thus, the high-speed imaging assemblies of the present invention provided acceptable images without the need to increase patient exposure to X-radiation (dosage).

TABLE II

Film	Screen	System Speed	Film Speed	Crossover	SSM @ 2 cycles/mm
A (Control)	Y	559	400	21%	0.24
B (Control)	X	620	600	21%	0.49
B (Control)	Y	865	600	21%	0.24
C (Invention)	X	826	800	8%	0.49
C (Invention)	Y	1154	800	8%	0.24

**Example 2:**

Cassettes used for imaging contained a pair of screens X, Y, or V on opposing sides of the noted Radiographic Films A, B, or C described in

## 5 Example 1.

Fluorescent intensifying screen "V" was a fluorescent intensifying screen that comprised a terbium activated gadolinium oxysulfide phosphor (median particle size of from 7.8 to 8  $\mu\text{m}$ ) dispersed in a Permuthane<sup>TM</sup> polyurethane binder in a single phosphor layer on a microvoided poly(ethylene terephthalate) film support. The total phosphor coverage was 9.2 g/dm<sup>2</sup> and the phosphor to binder weight ratio was 27:1. The screen speed was 600.

The microvoided support used in Screen V was prepared as a 3-layer film (with designated layers 1, 2 and 3) comprising voided polyester matrix layers. Materials used in the preparation of layers 1 and 3 of the film were a  
 15 compounded blend consisting of 60% by weight of barium sulfate (BaSO<sub>4</sub>) particles approximately 0.7  $\mu\text{m}$  in diameter (Blanc Fixe XR-HN available from Sachtleben Corp.) and 40% by weight PETG 6763 resin (IV=0.73 dl/g) (an amorphous polyester resin available from Eastman Chemical Company). The BaSO<sub>4</sub> inorganic particles were compounded with the PETG polyester by mixing  
 20 in a counter-rotating twin-screw extruder attached to a strand die. Strands of extrudate were transported through a water bath, solidified, and fed through a pelletizer, thereby forming pellets of the resin mixture. The pellets were then dried in a desiccant dryer at 65°C for 12 hours.

As the material for layer 2, poly(ethylene terephthalate) (#7352 from Eastman Chemicals Company) was dry blended with polypropylene ("PP", Huntsman P4G2Z-073AX) at 25% weight and dried in a desiccant dryer at 65°C for 12 hours.

5 Cast sheets of the noted materials were co-extruded to produce a combined support having the following layer arrangement: layer 1/layer 2/layer 3, using a 2.5 inch (6.35 cm) extruder to extrude layer 2, and a 1 inch (2.54 cm) extruder to extrude layers 1 and 3. The 275°C melt streams were fed into a 7 inch (17.8 cm) multi-manifold die also heated at 275°C. As the extruded sheet  
10 emerged from the die, it was cast onto a quenching roll set at 55°C. The PP in layer 2 dispersed into globules between 10 and 30 µm in size during extrusion. The final dimensions of the continuous cast multilayer sheet were 18 cm wide and 860 µm thick. Layers 1 and 3 were each 215 µm thick while layer 2 was 430 µm thick. The cast multilayer sheet was then stretched at 110°C first 3.0 times in the  
15 X-direction and then 3.4 times in the Y-direction. The stretched sheet was then heat set at 150°C and its final thickness was 175 µm.

A dispersion of green-emitting, terbium-doped gadolinium oxysulfide phosphor with a mean particle size of 6.8 µm was prepared from 100 g of the phosphor in a solution prepared from 117 g of polyurethane binder  
20 (trademark Permuthane U-6366) at 10 % (by weight) in a 93:7 volume ratio of dichloromethane and methanol. The resulting dispersion was coated at a phosphor coverage of 605 g/m<sup>2</sup> on the 3-layer reflective support noted above to produce Screen V.

Samples of the films in the three imaging assemblies were exposed  
25 and processed as described in Example 1. Optical densities are expressed below in terms of diffuse density as measured by a conventional X-rite Model 310TM densitometer that was calibrated to ANSI standard PH 2.19 and was traceable to a National Bureau of Standards calibration step tablet. The characteristic density vs. logE curve was plotted for each radiographic film that was exposed and processed  
30 as noted above. System speed was measured as noted above. Contrast (gamma) is the slope (derivative) of the density vs. logE sensitometric curve. SSM data for

the screens were determined as described above. Only the SSM values at 2 cycles/mm are reported in TABLE IV but FIG. 5 shows the SSM data over the entire range of spatial frequencies for Screen V in an imaging assembly of the present invention.

5                   FIG. 5 was generated from the following values shown in TABLE III:

TABLE III

SSM	Spatial Frequency (cycles/mm)
1.000	0
0.830	0.5
0.592	1.0
0.410	1.5
0.283	2.0
0.201	2.5
0.146	3.0
0.108	3.5
0.083	4.0
0.065	4.5
0.051	5.0
0.042	5.5
0.034	6.0
0.028	6.5
0.023	7.0
0.018	7.5
0.025	8.0
0.012	8.5
0.010	9.0
0.009	9.5
0.008	10.0

The following TABLE IV shows the sensitometric data of Films A-C when exposed with various screens. The data show that the overall system speeds when Films A and B are used can be increased by using higher-speed Screen Y. However, this increase in system speed results in a lower SSM value.

- 5 Film C, when used in combination with Screen X or Y, provided increased system speed. However, the imaging assembly containing Film C and Screen V provided the highest system speed with desired image quality. The % crossover was determined to be less than 8% for this imaging assembly.

10

TABLE IV

Film	Screen	Film Speed	System Speed	SSM @ 2 cycles/mm
A (Control)	X	400	400	0.49
A (Control)	Y	400	556	0.24
B (Control)	X	600	620	0.49
B (Control)	Y	600	865	0.24
C (Invention)	X	800	826	0.49
C (Invention)	Y	800	1154	0.24
C (Invention)	V	800	1322	0.28

### Example 3:

#### Radiographic Film D:

- 15 Radiographic Film D was a duplitized radiographic film with two different silver halide emulsion layers on each side of the support. The emulsion layers contained tabular silver halide grains that were dispersed in gelatin and were chemically sensitized with conventional sulfur-, gold-, and selenium-containing compounds using conventional procedures. Spectral sensitization to
- 20 the 530-570 nm region was provided using anhydro-5,5-dichloro-9-ethyl-3,3'-bis(3-sulfopropyl)oxacarbocyanine hydroxide (560 mg/mole of silver) followed by potassium iodide (400 mg/mole of silver). The emulsions of Film D were not prepared using oxidized gelatin.

Radiographic Film D had the following layer arrangement and formulations on the film support:

	Overcoat
	Interlayer
5	Emulsion Layer 1
	Emulsion Layer 2
	Support
	Emulsion Layer 2
	Emulsion Layer 1
10	Interlayer
	Overcoat

	<u>Overcoat Formulation</u>	<u>Coverage (mg/dm<sup>2</sup>)</u>
	Gelatin vehicle	3.4
15	Methyl methacrylate matte beads	0.14
	Carboxymethyl casein	0.57
	Colloidal silica (LUDOX AM)	0.57
	Polyacrylamide	0.57
	Chrome alum	0.025
20	Resorcinol	0.058
	Spermafol	0.15
	<u>Interlayer Formulation</u>	<u>Coverage (mg/dm<sup>2</sup>)</u>
	Gelatin vehicle	3.4
25	Carboxymethyl casein	0.57
	Colloidal silica (LUDOX AM)	0.57
	Polyacrylamide	0.57
	Chrome alum	0.025
	Resorcinol	0.058
30	Nitron	0.044

	<u>Emulsion Layer 1 Formulation</u>	<u>Coverage (mg/dm<sup>2</sup>)</u>
	Tabular grains	
	[AgBr 2.9 $\mu$ m ave. dia. x 0.10 $\mu$ m thickness]	9.1 Ag
	Gelatin vehicle	8.1
5	Microcrystalline Dye M-1 (shown above)	1.08
	4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene	2.1 g/Ag mole
	Potassium nitrate	1.1
	Ammonium hexachloropalladate	0.0013
10	Maleic acid hydrazide	0.0053
	Sorbitol	0.32
	Glycerin	0.35
	Potassium bromide	0.083
	Resorcinol	0.26
15	Bisvinylsulfonylmethane	2% based on total gelatin on same side

#### Radiographic Film E:

Radiographic Film E was a duplitized radiographic film with two different silver halide emulsion layers on each side of the support. The two emulsion layers contained tabular silver halide grains that were prepared and dispersed in oxidized gelatin that had been added at multiple times before and/or during the nucleation and early growth of the silver bromide tabular grains dispersed therein. The tabular grains in each silver halide emulsion layer had a mean aspect ratio of about 40. The nucleation and early growth of the tabular grains were performed using a "bromide-ion-concentration free-fall" process in which a dilute silver nitrate solution was slowly added to a bromide ion-rich deionized oxidized gelatin environment. The grains were chemically sensitized with sulfur, gold, and selenium using conventional procedures. Spectral

30

sensitization to about 560 nm was provided using anhydro-5,5-dichloro-9-ethyl-3,3'-bis(3-sulfopropyl)oxacarbocyanine hydroxide (680 mg/mole of silver) followed by potassium iodide (400 mg/mole of silver).

5	<u>Overcoat Formulation</u>	<u>Coverage (mg/dm<sup>2</sup>)</u>
	Gelatin vehicle	3.4
	Methyl methacrylate matte beads	0.14
	Carboxymethyl casein	0.57
	Colloidal silica (LUDOX AM)	0.57
10	Polyacrylamide	0.57
	Chrome alum	0.025
	Resorcinol	0.058
	Spermafol	0.15
15	<u>Interlayer Formulation</u>	<u>Coverage (mg/dm<sup>2</sup>)</u>
	Gelatin vehicle	3.4
	Carboxymethyl casein	0.57
	Colloidal silica (LUDOX AM)	0.57
	Polyacrylamide	0.57
20	Chrome alum	0.025
	Resorcinol	0.058
	Nitron	0.044
	<u>Emulsion Layer 1 Formulation</u>	<u>Coverage (mg/dm<sup>2</sup>)</u>
25	Tabular grains	
	[AgBr 4.0 µm ave. dia. x 0.10 µm thickness]	12.9 Ag
	Oxidized gelatin vehicle	2.2
	Non-oxidized gelatin vehicle	15
30	4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene	2.1 g/Ag mole
	Potassium nitrate	1.8

	Ammonium hexachloropalladate	0.0022
	Maleic acid hydrazide	0.0087
	Sorbitol	0.53
	Glycerin	0.57
5	Potassium bromide	0.14
	Resorcinol	0.44
	<u>Emulsion Layer 2 Formulation</u>	<u>Coverage (mg/dm<sup>2</sup>)</u>
	Tabular grain emulsion	
10	[AgBr 4.0 µm ave. dia. x 0.10 µm thickness]	6.5
	Oxidized gelatin vehicle	0.09
	Non-oxidized gelatin vehicle	1.1
	Microcrystalline Dye M-1 (shown above)	7.5
15	5-Bromide-4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene	0.7 g/Ag mole
	Potassium nitrate	1.1
	Ammonium hexachloropalladate	0.0013
	Maleic acid hydrazide	0.0053
	Sorbitol	0.32
20	Glycerin	0.35
	Potassium bromide	0.083
	Resorcinol	0.26
	Bisvinylsulfonylmethane	2% based on total gelatin on same side
25		

The cassettes used in the practice of this invention were those  
 commonly used in radiography and contained a pair of the films noted above and  
 of fluorescent intensifying screen X (noted above) on opposing sides of Films D  
 and E, to provide imaging assemblies.

Samples of Films D and E in the imaging assemblies were exposed and processed as described in Example 1.

Optical densities are expressed below in terms of diffuse density as measured by a conventional X-rite™ Model 310 densitometer that was calibrated to ANSI standard PH 2.19 and was traceable to a National Bureau of Standards calibration step tablet. The characteristic density vs. log E curve was plotted for each radiographic film that was exposed and processed as noted above. System speed, SSM values, and % crossover were measured using procedures like those described above. Only the SSM values at 2 cycles/mm are reported in TABLE VI but FIG. 6 shows the SSM data over the entire range of spatial frequencies for Screen X in an imaging assembly of the present invention.

FIG. 6 was generated from the following values shown in TABLE V:

TABLE V

SSM	Spatial Frequency (cycles/mm)
1.000	0
0.926	0.5
0.777	1.0
0.619	1.5
0.492	2.0
0.391	2.5
0.312	3.0
0.250	3.5
0.202	4.0
0.165	4.5
0.137	5.0
0.116	5.5
0.099	6.0
0.089	6.5
0.078	7.0

0.067	7.5
0.059	8.0
0.052	8.5
0.046	9.0
0.041	9.5
0.037	10.0

Contrast was measured as the slope of the Density vs. Log E sensitometric curve using conventional procedures.

- 5                   The following TABLE VI shows the sensitometric data of Radiographic Films A, B, D, and E when exposed with Screen X. The data show that the speed of the imaging assemblies was increased by using the higher speed Film B over Film A but contrast was not improved. The speed of the imaging assembly using Film D was not increased. Only the imaging assembly containing
- 10   Film E provided both an increase in speed and contrast.

TABLE VI

Film	Crossover	System Speed	Film Speed	Contrast	SSM @ 2 cycles/mm
A (Control)	20%	400	400	2.9	0.49
B (Control)	23%	620	600	2.9	0.49
D (Control)	6%	400	400	2.9	0.49
E (Invention)	6%	826	800	3.1	0.49

**Example 4:**

- 15                   Radiographic Films A and C (described in Example 1) and Film F were inserted into cassettes with a pair of various fluorescent intensifying screens X, Y, and Z to form imaging assemblies. Radiographic Film F was a sample of commercially available KODAK T-MAT<sup>®</sup> H radiographic film. Screens X and Y are defined above. Screen Z was a pair of asymmetric screens
- 20   that are commercially available as "Toshiba TO880". The screen speed was 780

and both screens contained terbium activated gadolinium oxysulfides as the phosphor in a binder. The frontside (exposure side) screen contained the phosphor at 8.1 mg/dm<sup>2</sup> and the backside screen had a phosphor coverage of 14.5 mg/dm<sup>2</sup>.

- 5                   The exposed film samples in the imaging assemblies were exposed and processed as described in Example 1 above. The resulting sensitometric properties (system speed and image contrast) were measured as described above and are shown in TABLE VII below. Only the SSM values at 2 cycles/mm are reported in TABLE VII. These data show that system speed can
- 10 be increased using a higher speed screen but resolution is diminished. The combination of Radiographic Film C and Screen X is advantageous because it requires the minimal amount of phosphor in the screens. The combination of Radiographic Film C and screen Z provided both much higher system speed and acceptable resolution.

15

TABLE VII

Film	Screen	System Speed	Total Phosphor (g/dm <sup>2</sup> , both sides)	Contrast	SSM @ 2 cycles/mm
A (Control)	X	400	9.66	2.9	0.28
A (Control)	Y	559	18.3	2.9	0.21
A (Control)	Z	800	22.6	2.9	0.15
F (Control)	X	600	9.66	2.7	0.28
C (Invention)	X	826	9.66	2.9	0.32
C (Invention)	Z	1600	22.6	2.9	0.18

**Claims:**

1. A radiographic imaging assembly that has a system speed of at least 800 and comprises:
  - A) a symmetric radiographic silver halide film having a film  
5 speed of at least 700 and comprising a support that has first and second major surfaces,  
said radiographic silver halide film having disposed on said first major support surface, two or more hydrophilic colloid layers including first and second silver halide emulsion layers, and having on said second major support  
10 surface, two or more hydrophilic colloid layers including third and fourth silver halide emulsion layers, said first and third silver halide emulsion layers being the outermost emulsion layers on their respective sides of said support,  
said second and fourth silver halide emulsion layers comprising a crossover control agent sufficient to reduce crossover to less than 15%, and  
15 B) a fluorescent intensifying screen arranged on each side of said radiographic silver halide film, the pair of screens having a screen speed of at least 400 and said screens having an average screen sharpness measurement value greater than reference Curve A of FIG. 4, and each screen comprising an inorganic phosphor capable of absorbing X-rays and emitting electromagnetic radiation  
20 having a wavelength greater than 300 nm, said inorganic phosphor being coated in admixture with a polymeric binder in a phosphor layer on a support.
2. The imaging assembly of claim 1 wherein each of said first, second, third, and fourth silver halide emulsion layers comprising tabular silver  
25 halide grains that have the same or different composition and independently an aspect ratio of at least 15 and an average diameter of at least 3.0  $\mu\text{m}$ , and comprise at least 50 mol % bromide and up to 5 mol % iodide, both based on total silver in said grains,
- 30 3. The imaging assembly of claim 2 wherein said tabular silver halide grains in said first, second, third, and fourth silver halide emulsion layers

are composed of at least 90 mol % bromide and up to 1 mol % iodide, both based on total silver in the emulsion layer, an aspect ratio of from 25 to 45, an average diameter of at least 3.5  $\mu\text{m}$ , and independently an average thickness of from 0.06 to 0.16  $\mu\text{m}$ .

5

4. The imaging assembly of claim 1 wherein said tabular silver halide grains in said first, second, third, and fourth silver halide emulsion layers are dispersed in a hydrophilic polymeric vehicle mixture comprising at least 0.05% of oxidized gelatin, based on the total dry weight of said polymeric vehicle mixture.

10

5. The imaging assembly of claim 4 wherein said tabular silver halide grains in said first, second, third, and fourth silver halide emulsion layers are dispersed in from 1 to 15% deionized oxidized gelatin, based on the total dry weight of said polymeric vehicle mixture.

15

6. The radiographic imaging assembly of claim 1 wherein the molar ratio of silver in said first silver halide emulsion layer to that of said second silver halide emulsion layer is greater than 1:1, and the molar ratio of silver in said third silver halide emulsion layer to that of said fourth silver halide emulsion layer is independently greater than 1:1, the amount polymer vehicle on each side of said support is from 20 to 40  $\text{mg}/\text{dm}^2$ , and the level of silver on each side of said support is from 10 to 25  $\text{mg}/\text{dm}^2$ .

20

7. The imaging assembly of claim 1 wherein said crossover control agent in said radiographic silver halide film is present in an amount sufficient to reduce crossover to less than 12%.

25

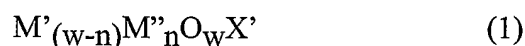
8. The imaging assembly of claim 1 wherein said crossover control agent is a particulate merocyanine or oxonol dye that is present in each of

30

said second and fourth silver halide emulsion layers in an amount of from 0.75 to 1.5 mg/m<sup>2</sup>.

9. The imaging assembly of claim 1 wherein said inorganic  
5 phosphor is:

a) a rare earth oxychalcogenide and oxyhalide phosphor that is represented by the following formula (1):

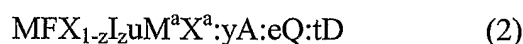


wherein M' is at least one of the metals yttrium (Y), lanthanum (La), gadolinium  
10 (Gd), or lutetium (Lu), M'' is at least one of the rare earth metals, preferably dysprosium (Dy), erbium (Er), europium (Eu), holmium (Ho), neodymium (Nd), praseodymium (Pr), samarium (Sm), tantalum (Ta), terbium (Tb), thulium (Tm), or ytterbium (Yb), X' is a middle chalcogen (S, Se, or Te) or halogen, n is 0.002 to 0.2, and w is 1 when X' is halogen or 2 when X' is a middle chalcogen,

15 b) a lanthanum oxybromides,

c) a terbium-activated or thulium-activated gadolinium oxide or oxysulfides, or

d) an alkaline earth metal phosphor that is the product of firing starting materials comprising optional oxide and a combination of species  
20 characterized by the following formula (2):



wherein "M" is magnesium (Mg), calcium (Ca), strontium (Sr), or barium (Ba), "F" is fluoride, "X" is chloride (Cl) or bromide (Br), "I" is iodide, M<sup>a</sup> is sodium (Na), potassium (K), rubidium (Rb), or cesium (Cs), X<sup>a</sup> is fluoride (F), chloride  
25 (Cl), bromide (Br), or iodide (I), "A" is europium (Eu), cerium (Ce), samarium (Sm), or terbium (Tb), "Q" is BeO, MgO, CaO, SrO, BaO, ZnO, Al<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, GeO<sub>2</sub>, SnO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>, or ThO<sub>2</sub>, "D" is vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), or nickel (Ni), "z" is 0 to 1, "u" is from 0 to 1, "y" is from 1 x 10<sup>-4</sup> to 0.1, "e" is from 0 to 1, and "t" is  
30 from 0 to 0.01.

10. The imaging assembly of claim 1 wherein said inorganic phosphor is a terbium activated gadolinium oxysulfide.

11. The imaging assembly of claim 1 wherein said fluorescent intensifying screen support comprises a reflective substrate comprising a continuous polyester first phase and second phase dispersed within said continuous polyester first phase, said second phase comprised of microvoids containing inorganic particles.

12. The imaging assembly of claim 11 wherein said inorganic particles are barium sulfate particles.

13. The imaging assembly of claim 11 wherein the reflective index of said polyester first phase to said second phase is from 1.4:1 to 1.6:1, said microvoids occupy from 35 to 60% (by volume) of said reflective substrate, said reflective support has a dry thickness of from 100 to 400 nm, and the average barium sulfate particle size is from 0.6 to 2  $\mu\text{m}$  and comprise from 35 to 65 weight % of the total substrate weight.

14. A radiographic imaging assembly having a system speed of at least 1100 and comprising:

A) a symmetric radiographic silver halide film having a film speed of at least 800 and comprising a support that has first and second major surfaces,  
said radiographic silver halide film having disposed on said first major support surface, two or more hydrophilic colloid layers including first and second silver halide emulsion layers, and having on said second major support surface, two or more hydrophilic colloid layers including third and fourth silver halide emulsion layers, said first and third silver halide emulsion layers being the outermost emulsion layers on their respective sides of said support,

each of said first, second, third, and fourth silver halide emulsion layers comprising tabular silver halide grains that have the same composition, independently an aspect ratio of from 38 to 45, an average diameter of at least 3.5  $\mu\text{m}$ , and an average thickness of from 0.08 to 0.14  $\mu\text{m}$ , and comprise at least 95  
5 mol % bromide and up to 0.1 mol % iodide, both based on total silver in said grains,

each of said second and fourth silver halide emulsion layers comprising a particulate oxonol dye as a crossover control agent present in an amount of from 1 to 1.3  $\text{mg}/\text{m}^2$  that is sufficient to reduce crossover to less than  
10 12% and that is decolorized during development within 45 seconds,

said film further comprising a protective overcoat on both sides of said support disposed over all of said silver halide emulsion layers,

wherein said tabular silver halide grains in said first, second, third, and fourth silver halide emulsion layers are dispersed in a hydrophilic polymeric  
15 vehicle mixture comprising from 5 to 15% of deionized oxidized gelatin, based on the total dry weight of said polymeric vehicle mixture,

wherein the dry, unprocessed thickness ratio of said first silver halide emulsion layer to that of said second silver halide emulsion layer is from 3:1 to 1:1, and the dry, unprocessed thickness ratio of said third silver halide  
20 emulsion layer to that of said fourth silver halide emulsion layer is independently from 3:1 to 1:1, and

wherein the molar ratio of silver in said first silver halide emulsion layer to that of said second silver halide emulsion layer is from 1.5:1 to 3:1, and the molar ratio of silver in said third silver halide emulsion layer to that of said  
25 fourth silver halide emulsion layer is independently from 1.5:1 to 3:1, and

B) a fluorescent intensifying screen arranged on both sides of said film, the pair of screens having a screen speed of at least 600 and said screens having an average screen sharpness measurement (SSM) value that is at least 1.1 that of reference Curve A of FIG. 4 at a given spatial frequency, and each screen  
30 comprising a terbium activated gadolinium oxysulfide phosphor capable of absorbing X-rays and emitting electromagnetic radiation having a wavelength

greater than 300 nm, said phosphor being coated in admixture with a polymeric binder in a phosphor layer on a flexible polymeric support.

15           15.     The imaging assembly of claim 14 wherein said flexible  
polymeric support comprises a reflective substrate comprising a continuous  
biaxially oriented polyester first phase and second phase dispersed within said  
continuous polyester first phase, said second phase comprised of microvoids  
occupying from 35 to 60% (by volume) of said reflective substrate, and said  
10     microvoids containing barium sulfate particles that have an average particle size of  
from 0.06 to 2  $\mu\text{m}$  and comprise from 35 to 65 weight % of the total substrate  
weight.

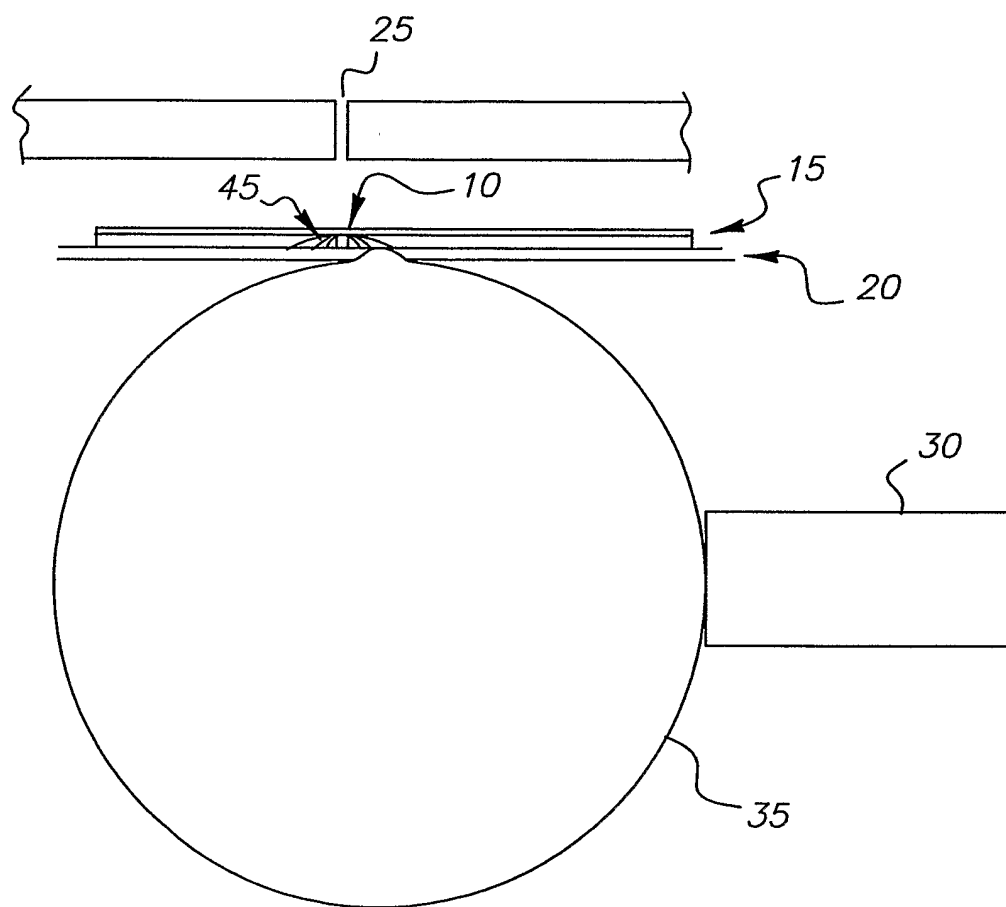
            16.     The imaging assembly of claim 14 wherein said polyester  
first phase is biaxially oriented poly(1,4-cyclohexylene dimethylene terephthalate)  
15     or poly(ethylene terephthalate).

            17.     A method of providing a black-and-white image comprising  
exposing the radiographic silver halide film in the radiographic imaging assembly  
of claim 1 and processing said film, sequentially, with a black-and-white  
20     developing composition and a fixing composition.

            18.     A method of providing a black-and-white image comprising  
exposing the radiographic silver halide film in the radiographic imaging assembly  
of claim 14 and processing said film, sequentially, with a black-and-white  
25     developing composition and a fixing composition.

            19.     The method of claim 17 further comprising using said  
black-and-white image for a medical diagnosis.

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*FIG. 1*

2/5

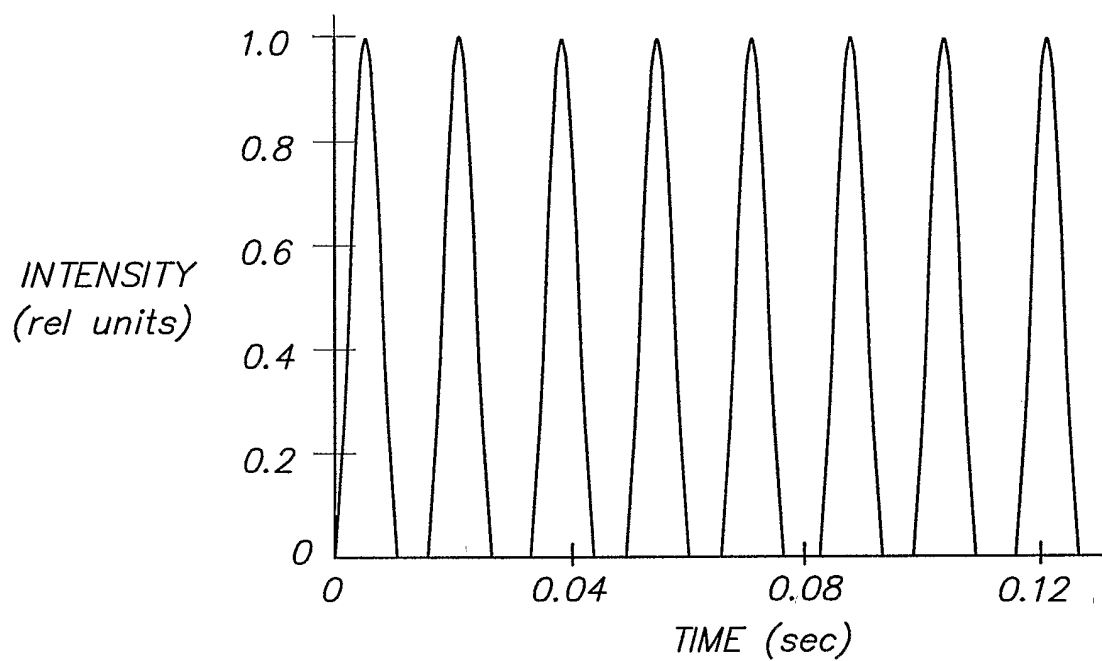


FIG. 2

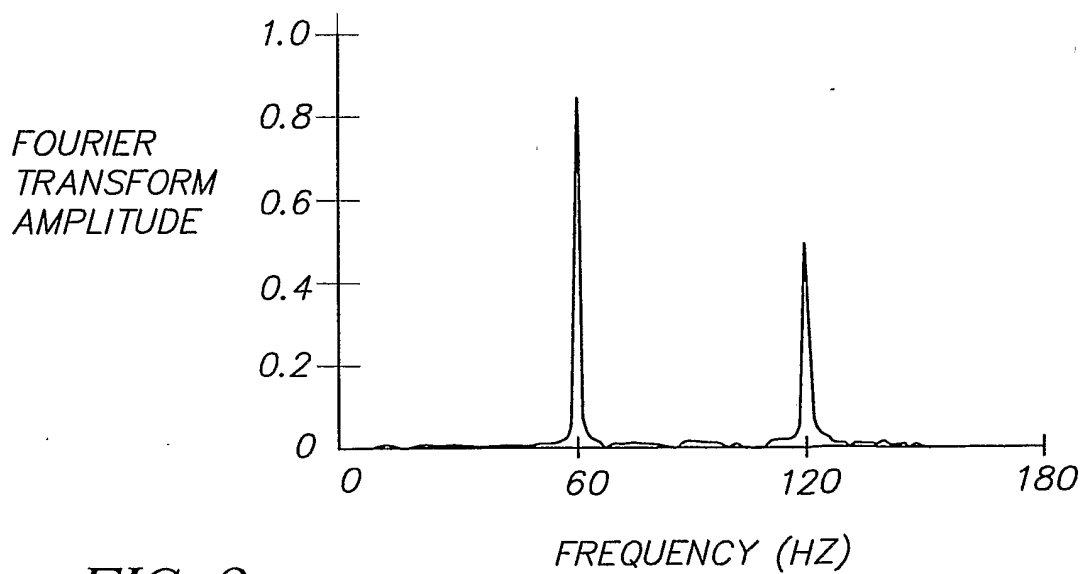


FIG. 3

3/5

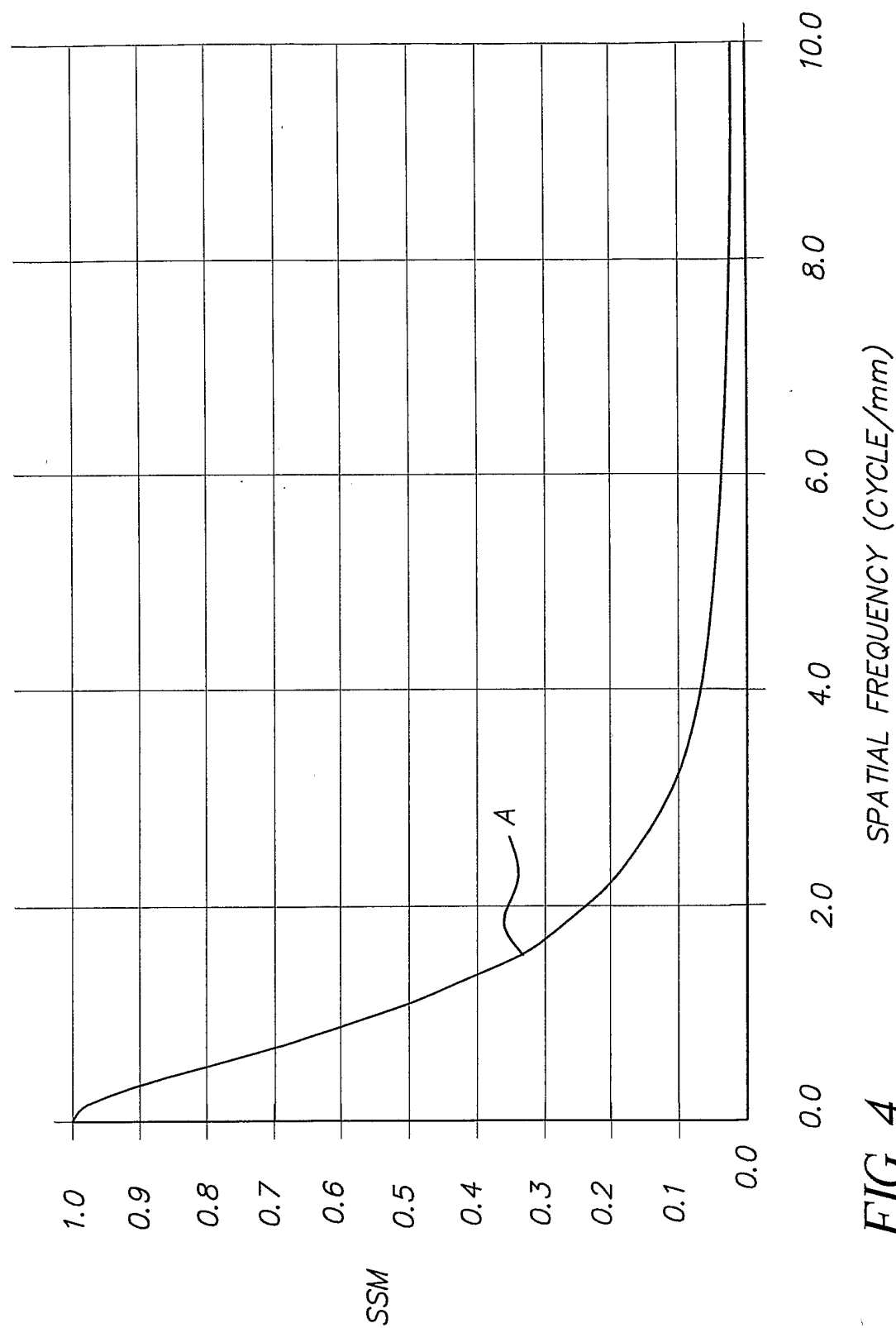


FIG. 4

4/5

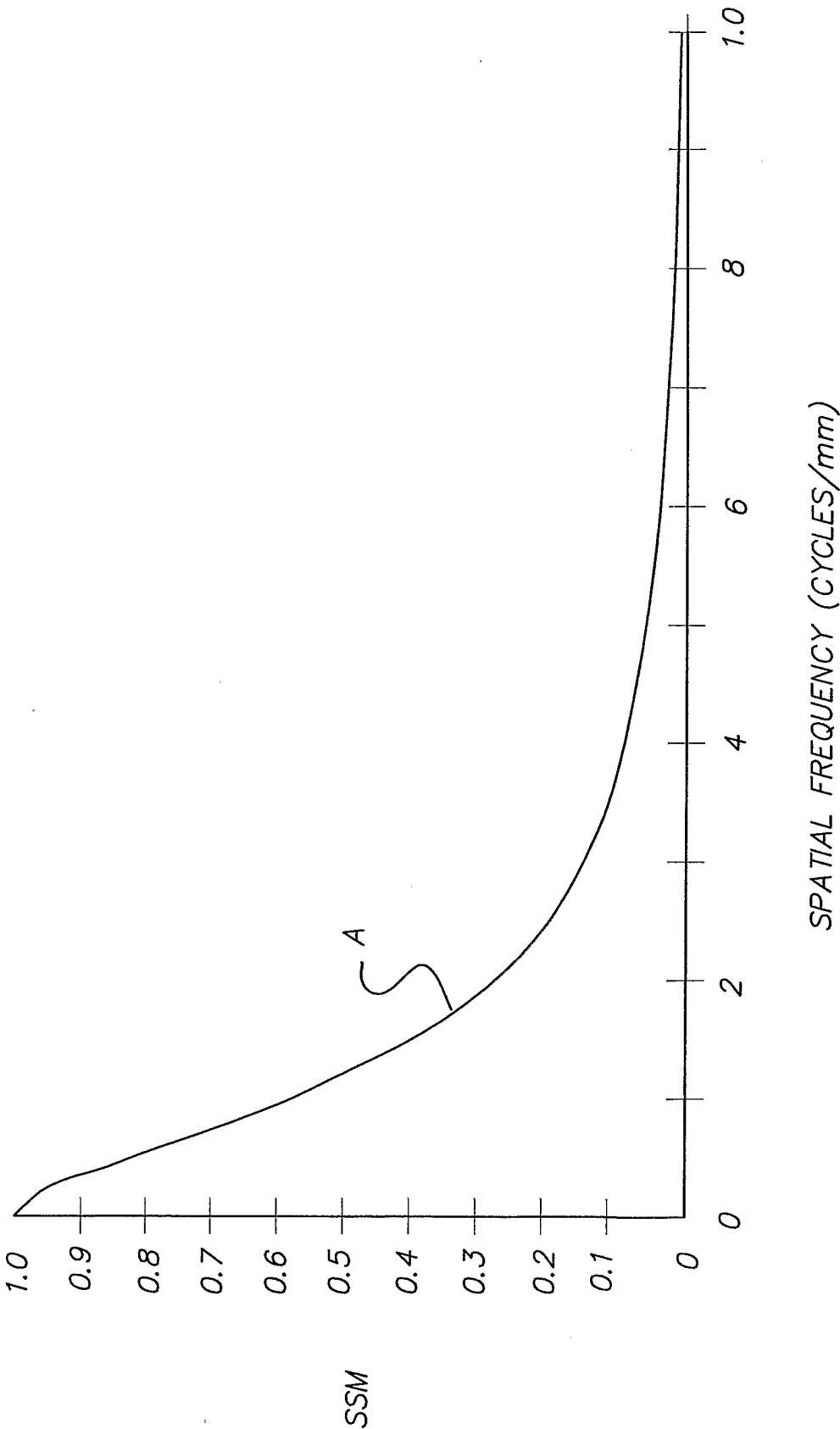


FIG. 5

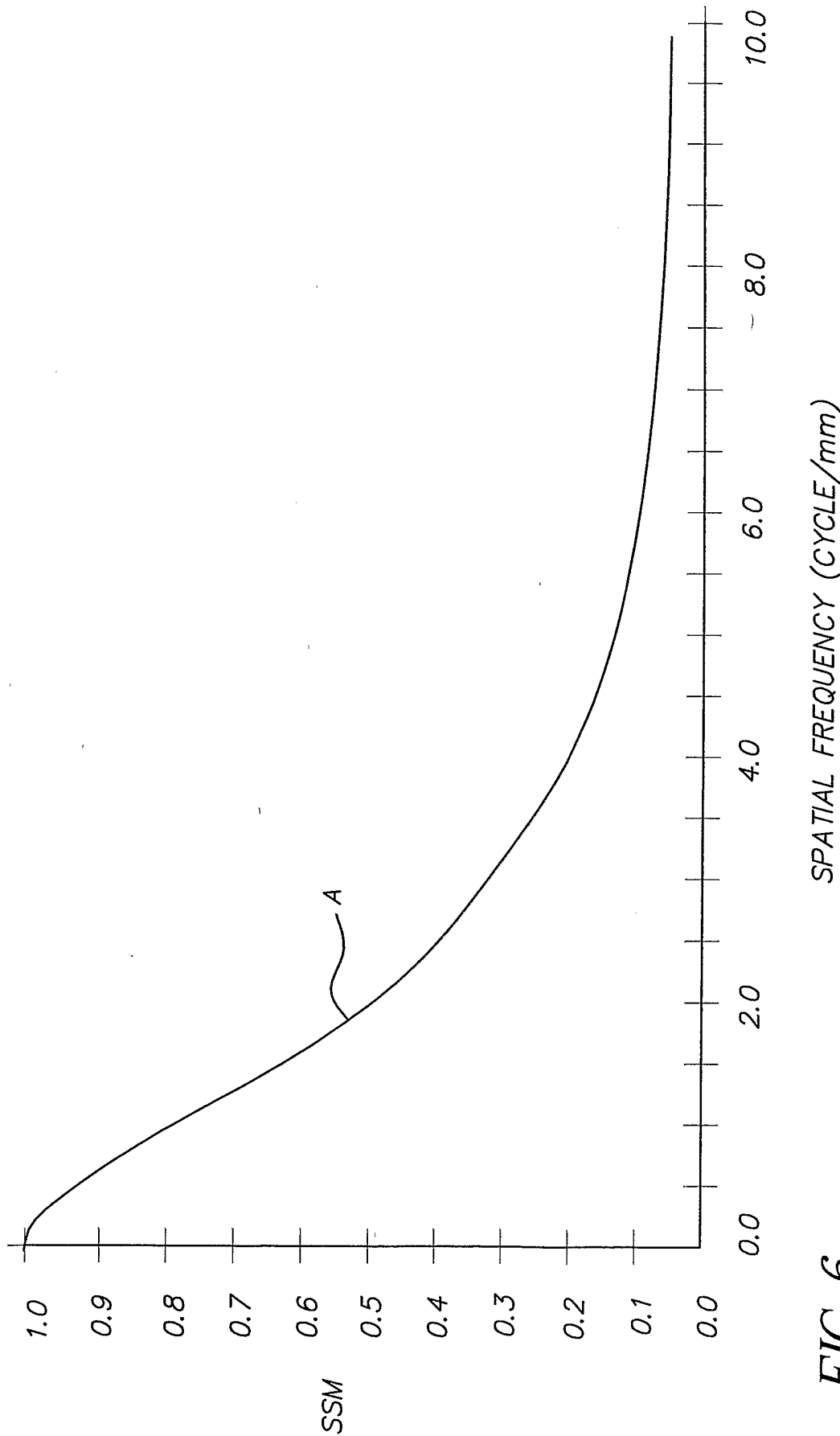


FIG. 6

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2004/037174

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G03C5/17

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 203 985 A (EASTMAN KODAK COMPANY) 8 May 2002 (2002-05-08) claim 1 paragraph '0076! -----	1-19
X	US 2002/155373 A1 (DICKERSON ROBERT E ET AL) 24 October 2002 (2002-10-24) claim 1 paragraph '0099! -----	1-19
X	US 6 350 554 B1 (DICKERSON ROBERT E ET AL) 26 February 2002 (2002-02-26) claim 1 column 11, line 50 - line 65 ----- -/--	1-19



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

International Application No

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