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(54) **Film with blue dye**

(57) An imaging element having a polymer support, a blue dye sufficient to result in a CIELAB measurement of L* less than or equal to 80 and a b* less than or equal to -25.

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Description**FIELD OF THE INVENTION**

5 **[0001]** The invention relates generally to film, imaging, and the field of radiography, particularly X-ray radiography. More specifically, the invention relates to blue tinted X-ray films.

BACKGROUND OF THE INVENTION

10 **[0002]** Over one hundred years ago, W. C. Roentgen discovered X-radiation by the exposure of a silver halide imaging element. In 1913, Eastman Kodak Company introduced its first product specifically intended to be exposed by X-radiation (X-rays). _Today, radiographic silver halide films account for the overwhelming majority of medical diagnostic images. _Such films provide viewable black-and-white images upon imagewise exposure followed by processing with the suitable wet developing and fixing photochemicals.

15 **[0003]** In medical radiography an image of a patient's anatomy is produced by exposing the patient to X-rays and recording the pattern of penetrating X-radiation using a radiographic film containing at least one radiation-sensitive silver halide emulsion layer coated on a transparent support. An approach to reducing patient exposure is to employ one or more phosphor-containing intensifying screens in combination with the radiographic film (usually both in the front and back of the film). _An intensifying screen absorbs X-rays and emits longer wavelength electromagnetic radiation that
20 the silver halide emulsions more readily absorb.

[0004] Another technique for reducing patient exposure is to coat two silver halide emulsion layers on opposite sides of the film support to form a "dual coated" radiographic film so the film can provide suitable images with less exposure. _Of course, a number of commercial products provide assemblies of both dual coated films in combination with two intensifying screens to allow the lowest possible patient exposure to X-rays. _Typical arrangements of film and screens
25 are described in considerable detail for example in U.S. Pat. No. 4,803,150 (Dickerson et al.), U.S. Pat. No. 5,021,327 (Bunch et al.), and U.S. Pat. No. 5,576,156 (Dickerson).

[0005] Medical radiographic X-radiation films are currently manufactured with several different contrasts in order to meet the diverse radiographic imaging needs. _These include high contrast films such as commercially available Carestream Health TMAT-G Film and low contrast films such as Carestream Health TMAT-L Film. _High contrast films are
30 designed to image anatomy parts that exhibit a narrow range of X-radiation absorbance (such as bones). _Medium and low contrast films are designed to image simultaneously several different types of anatomy having different X-radiation absorbance. _Radiography of the thoracic cavity (chest) is an example of this need where radiologists need to image the relatively radio-opaque mediastinal area (behind the vertebral column, heart and diaphragm). _These areas are quite dense and require greater amounts of X-radiation for desired penetration and imaging on a film. _However, it is
35 also desired to image the more radio-transparent lungs. Such imaging requires less X-radiation. _Carestream Health InSight™ IT Film and Carestream Health InSight™ VHC Film, and the appropriate intensifying screens, are low crossover systems designed to record this wide range of tissue densities with high imaging quality and varying exposure latitude.

[0006] X-ray radiographic films containing blue-tinted dyes have been utilized for several decades. _The reason for such dyes is to improve the image tone of the resulting radiographic images. _Radiographic images formed by exposure
40 to X-rays on an X-ray radiographic film consists of silver deposits that have a yellow-brown appearance which is objectionable to many radiologists. The resulting color from the developed silver can be measured using spectral absorption techniques, and is measured as a higher absorbance in the blue portion of the visible spectrum. In order to compensate for this color, blue-tinting dyes are added to the film, thereby increasing the spectral absorbance in the green and red portions of the visible spectrum. The result is a radiograph with an acceptable blue-red appearance.

45 **[0007]** Addition of blue-tinting dye also has the effect of increasing film Dmin or total density of the unexposed or low-exposure region of a processed radiographic film. The Dmin value, as measured after film exposure and processing, is generally considered to contain at least the following two factors: (1) an optical density due to the support and tinting dyes that is present before and after processing, and (2) an optical density resulting from the processing itself. For the purpose of discussing this invention, factor (2) is conventional silver fog. The Dmin value of a radiograph is a primary
50 criterion for acceptable performance of a radiographic film in customer usage, as established by various standards committees that monitor performance of X-ray films in the field of medical radiography. _These standard committees can be local, statewide or even national organizations that set limits on various film parameters that measure the performance of X-ray films. _It is generally accepted that lower Dmin value yields an improved radiograph, with higher image quality for reading details and features. Several standards committees have set limits on film D-min to be as low
55 as 0.25 or 0.30 for the whole lifetime of a film. _These low Dmin specifications often result in reduced expiration dating of a film because the Dmin from silver fog increases with age.

[0008] US Patent No. 1,973,886 (Scanlan) describes an X-ray film including the addition of a blue tint to an X-ray base material.

[0009] US Patent No. 5,851,243 (Dickerson) patent describes the addition of a blue dye to increase neutral density in minimum density areas of an X-ray film.

[0010] US Patent No. 6,517,986 (Dickerson) describes the a^* and b^* values of a X-ray film containing colorants.

[0011] The publication "New Discoveries in Vision Effect Lighting Practice" by Sam M. Berman of Lawrence Berkeley National Laboratory in Berkeley, CA 94720 describes discoveries concerning photosensitivity of the eye.

[0012] There remains a need for improved X-ray films. In particular, there is a need for improved films for use with mammography and general-purpose radiography. Such films would have improved visual contrast, improved image quality, and/or provide the capability of improved radiographic or radiologic diagnosis.

SUMMARY OF THE INVENTION

[0013] An object of the present invention is to produce improved X-ray films.

[0014] Another object of the present invention is to produce X-ray film with improved contrast.

[0015] Yet another object of the present invention is to produce X-ray film with improved image quality.

[0016] Yet another object of the present invention is to produce X-ray film with the capability of improved radiographic or radiologic diagnosis.

[0017] These objects are given only by way of illustrative example, and such objects may be exemplary of one or more embodiments of the invention. Other desirable objectives and advantages inherently achieved by the disclosed invention may occur or become apparent to those skilled in the art. The invention is defined by the appended claims.

[0018] According to one aspect of the invention, there is provided an imaging element comprising a polymer support, a blue dye sufficient to result in a CIELAB measurement of L^* less than or equal to 80 and a b^* less than or equal to -25.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] The foregoing and other objects, features, and advantages of the invention will be apparent from the following more particular description of the embodiments of the invention, as illustrated in the accompanying drawings.

[0020] The elements of the drawings are not necessarily to scale relative to each other.

FIG. 1 shows transmittance of an imaging support.

FIG. 2 shows sensitivity of the eye.

FIG. 3 shows optical characteristics of commercial films.

FIG. 4 shows optical characteristics of commercial films.

DETAILED DESCRIPTION OF THE INVENTION

[0021] The following is a detailed description of the preferred embodiments of the invention.

[0022] While the invention is being described with regard to radiography, those skilled in the art will recognize that the invention can be applied to other imaging applications, for example, business imaging.

[0023] The CIELAB b^* values describe the yellowness vs. blueness of an image with more positive values indicating a tendency toward greater yellowness, CIELAB a^* values compare greenness vs. redness, where more positive values indicating a higher proportion toward redness. CIELAB L^* or luminosity is a measure of how much light is transmitted from an object to the eye. L^* , a^* and b^* measurement techniques are described by Billmeyer and Saltzman, Principles of Color Technology, 2nd. Ed., Wiley, New York, 1981, at Chapter 3. The measurements of a^* and b^* were developed by the Commission Internationale de L'Esclairage (International Commission on Illumination).

[0024] The invention allows a formation of an improved X-ray film. The inventive X-ray film has better contrast, particularly for utilization in mammography as well as other uses. The inventive X-ray film has improved image quality. The inventive X-ray film has the capability for improved radiographic or radiologic diagnosis. The film utilizes materials similar to those materials already in the X-ray film but in different quantities to achieve an improved result at low cost. The improved X-ray further can be utilized in the present machines for taking X-rays and for developing the X-rays.

[0025] Where two or more silver halide emulsions are disposed on each side of the film support, the "bottom" silver halide emulsion layer is closest to the film support and is defined herein as the "first" or "third" emulsion depending upon which side of the support it resides. The "top" silver halide emulsion layer is farther from the film support and is defined herein as the second or fourth emulsion depending upon which side of the support it resides. Thus, the "first" and "second" silver halide emulsion layers are on one side of the support and the "third" and "fourth" silver halide emulsion layers are on the opposite side of the support.

[0026] The radiographic films of this invention include a flexible support having disposed on both sides thereof one or more silver halide emulsion layers and optionally one or more non-radiation sensitive hydrophilic layer(s). The silver halide emulsions in the various layers can be the same or different, and can comprise mixtures of various silver halide

emulsions in or more of the layers.

[0027] In preferred embodiments, the film has the same single silver halide emulsion layer on both sides of the support. It is also preferred that the films have a protective overcoat (described below) over the silver halide emulsion on each side of the support.

[0028] The support can take the form of any conventional imaging or radiographic element support that is X-radiation and light transmissive. Useful transparent supports for the films of this invention can be chosen from among those described in Research Disclosure, September 1996, Item 38957 XV. Supports and Research Disclosure, Vol. 184, August 1979, Item 18431, XII. Film Supports. Research Disclosure is published by Kenneth Mason Publications, Ltd., Dudley House, 12 North Street, Emsworth, Hampshire PO10 7DQ England.

[0029] In its simplest possible form the transparent film 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 film is itself hydrophobic and subbing layers are coated on the film to facilitate adhesion of the hydrophilic silver halide emulsion layers. Typically the film support is either colorless or blue tinted (tinting dye being present in one or both of the support film and the subbing layers). Referring to Research Disclosure, Item 38957, Section XV Supports, cited above, attention is directed particularly to paragraph (2) that describes subbing layers, and paragraph (7) that describes preferred polyester film supports.

[0030] In the more preferred embodiments, at least one non-light sensitive hydrophilic layer is included with the one or more silver halide emulsion layers on each side of the film support. This layer may be called an interlayer or overcoat, or both.

[0031] The silver halide emulsion layers comprise one or more types of silver halide grains responsive to X-radiation. Silver halide grain compositions particularly contemplated include those having at least 80 mol % bromide (preferably at least 98 mol % bromide) based on total silver in a given emulsion layer. Such emulsions include silver halide grains composed of, for example, silver bromide, silver iodobromide, silver chlorobromide, silver iodochlorobromide, and silver chloriodobromide. Iodide is generally limited to no more than 3 mol % (based on total silver in the emulsion layer) to facilitate more rapid processing. Preferably iodide is from 0 to 1.5 mol % (based on total silver in the emulsion layer) or eliminated entirely from the grains. The silver halide grains in each silver halide emulsion layer can be the same or different, or mixtures of different types of grains.

[0032] The silver halide grains useful in this invention can have any desirable morphology including, but not limited to, cubic, octahedral, tetradecahedral, rhombic, orthorhombic, rounded, spherical or other non-tabular morphologies, or be comprised of a mixture of two or more of such morphologies. Some films may be prepared by emulsions for which at least 50% of the total grain projected area within each silver halide emulsion layer is provided by tabular grains. Preferably, substantially all of the grains are tabular grains in each silver halide emulsion layer.

[0033] Thus, different silver halide emulsion layers can have silver halide grains of the same or different morphologies as long as at least 50% of the grains are tabular grains. Some imaging layers use cubic emulsions, where the grains generally have an ECD of at least 0.5 μm and less than 2 μm (preferably from about 0.6 to about 1.4 μm). The useful ECD values for other non-tabular morphologies would be readily apparent to a skilled artisan in view of the useful ECD values provided for cubic and tabular grains.

[0034] Generally, the average ECD of tabular grains used in the films is greater than 0.6 μm and less than 5 μm , and preferably greater than 0.7 and less than 3 μm . Most preferred ECD values are from about 1.0 to about 3.0 μm . The average thickness of the tabular grains used in this invention is generally at least 0.04 and no more than 0.13 μm , and preferably at least 0.06 and no more than 0.12 μm .

[0035] It may also be desirable to employ silver halide grains that exhibit a coefficient of variation (COV) of grain ECD of less than 20% and, preferably, less than 10%. In some embodiments, such as in mammography, it may be desirable to employ a grain population that is as highly monodisperse as can be conveniently realized. A highly monodispersed grain population has a very low COV, preferably below 20%.

[0036] Generally, at least 50% (and preferably at least 80%) of the silver halide grain projected area in each silver halide emulsion layer is provided by tabular grains having an average aspect ratio greater than 5, and more preferably greater than 8.

[0037] Tabular grain emulsions that have the desired composition and sizes are described in greater detail in the following patents, the disclosures of which are incorporated herein by reference: U.S. Patent No. 4,414,310 (Dickerson), U.S. Patent No. 4,425,425 (Abbott et al.), U.S. Patent No. 4,425,426 (Abbott et al.), U.S. Patent No. 4,439,520 (Kofron et al.), U.S. Patent No. 4,434,226 (Wilgus et al.), U.S. Patent No. 4,435,501 (Maskasky), U.S. Patent No. 4,713,320 (Maskasky), U.S. Patent No. 4,803,150 (Dickerson et al.), U.S. Patent No. 4,900,355 (Dickerson et al.), U.S. Patent No. 4,994,355 (Dickerson et al.), U.S. Patent No. 4,997,750 (Dickerson et al.), U.S. Patent No. 5,021,327 (Bunch et al.), U.S. Patent No. 5,147,771 (Tsaur et al.), U.S. Patent No. 5,147,772 (Tsaur et al.), U.S. Patent No. 5,147,773 (Tsaur et al.), U.S. Patent No. 5,171,659 (Tsaur et al.), U.S. Patent No. 5,252,442 (Dickerson et al.), U.S. Patent No. 5,370,977 (Zietlow), U.S. Patent No. 5,391,469 (Dickerson), U.S. Patent No. 5,399,470 (Dickerson et al.), U.S. Patent No. 5,411,853 (Maskasky), U.S. Patent No. 5,418,125 (Maskasky), U.S. Patent No. 5,494,789 (Daubendiek et al.), U.S. Patent No.

5,503,970 (Olm et al.), U.S. Patent No. 5,536,632 (Wen et al.), U.S. Patent No. 5,518,872 (King et al.), U.S. Patent No. 5,567,580 (Fenton et al.), U.S. Patent No. 5,573,902 (Daubendiek et al.), U.S. Patent No. 5,576,156 (Dickerson), U.S. Patent No. 5,576,168 (Daubendiek et al.), U.S. Patent No. 5,576,171 (Olm et al.), and U.S. Patent No. 5,582,965 (Deaton et al.).

[0038] The patents to Abbott et al., Fenton et al., Dickerson, and Dickerson et al. are also cited and incorporated herein to show conventional radiographic film features in addition to gelatino-vehicle, high bromide (greater than or equal to 80 mol % bromide based on total silver) tabular grain emulsions and other features useful in the present invention.

[0039] A variety of silver halide dopants can be used, individually and in combination, to improve contrast as well as other common properties, such as speed and reciprocity characteristics. A summary of conventional dopants to improve speed, reciprocity and other imaging characteristics is provided by Research Disclosure, Item 38957, cited above, Section 1. Emulsion grains and their preparation, sub-section D. Grain modifying conditions and adjustments, paragraphs (3), (4), and (5).

[0040] A general summary of silver halide emulsions and their preparation is provided by Research Disclosure, Item 38957, cited above, Section 1. 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, cited above, Section III. Emulsion washing.

[0041] 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 are specifically contemplated. Sulfur sensitization is preferred, and can be carried out using for example, thiosulfates, thiosulfonates, thiocyanates, isothiocyanates, thioethers, thioureas, cysteine, or rhodanine. A combination of gold and sulfur sensitization is most preferred.

[0042] 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 illustrated by Research Disclosure, Item 38957, Section VII. Antifoggants and stabilizers, and Item 18431, Section II: Emulsion Stabilizers, Antifoggants and Antikinking Agents.

[0043] The silver halide emulsion layers and other hydrophilic layers on both sides of the support of the radiographic film generally contain conventional polymer vehicles (peptizers and binders) that include both synthetically prepared and naturally occurring colloids or polymers. The most preferred polymer 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 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). Cationic starch used as a peptizer for tabular grains is described in U.S. Pat. No. 5,620,840 (Maskasky) and U.S. Pat. No. 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 and polyacrylamides (including polymethacrylamides). Dextrans can also be used. Examples of such materials are described for example in U.S. Pat. No. 5,876,913 (Dickerson et al.), incorporated herein by reference.

[0044] The silver halide emulsion layers (and other hydrophilic layers) in the radiographic films of this invention are generally fully hardened using one or more conventional hardeners. Thus, the amount of hardener on each side of the support is generally at least 0.3% and up to 1% (preferably up to 0.8%), based on the total dry weight of the polymer vehicles on that side of the support.

[0045] Conventional hardeners can be used for this purpose, including but not limited to formaldehyde and free dialdehydes such as succinaldehyde and glutaraldehyde, blocked dialdehydes, .alpha.-diketones, active esters, sulfonate esters, active halogen compounds, s-triazines and diazines, epoxides, aziridines, active olefins having two or more active bonds, blocked active olefins, carbodiimides, isoxazolium salts unsubstituted in the 3-position, esters of 2-alkoxy-N-carboxyhydroquinoline, N-carbamoyl pyridinium salts, carbamoyl oxypyridinium salts, bis (amidino) ether salts, particularly bis(amidino) ether salts, surface-applied carboxyl-activating hardeners in combination with complex-forming salts, carbamoylonium, carbamoyl pyridinium and carbamoyl oxypyridinium salts in combination with certain aldehyde scavengers, dication ethers, hydroxylamine esters of imidic acid salts and chloroformamidinium salts, hardeners of mixed function such as halogen-substituted aldehyde acids (e.g., mucochloric and mucobromic acids), onium-substituted acroleins, vinyl sulfones containing other hardening functional groups, polymeric hardeners such as dialdehyde starches, and copoly(acrolein-methacrylic acid).

[0046] In one embodiment of the invention, each side of the radiographic film support contains silver at level that is generally at least 8 and no more than 20 mg/dm², and preferably at least 11 and no more than 13 mg/dm². In addition, the total coverage of polymer vehicle in each silver halide emulsion layer is generally at least 7 and no more than 20

mg/dm² and preferably no more than 15 mg/dm².

[0047] In other embodiments of the invention, such as mammography, dental, and non-destructive-testing, silver and gel levels may be higher.

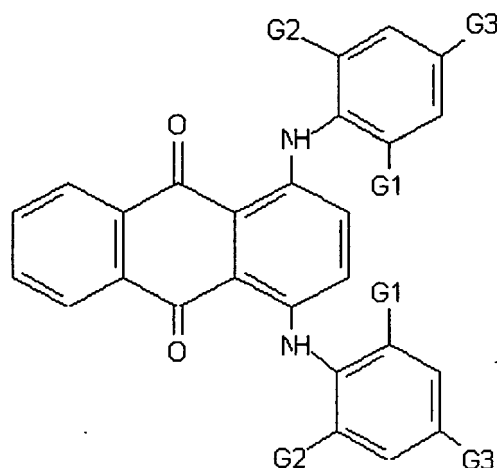
[0048] There will be other polymer vehicle amounts in the various non-silver layers on each side of the support. The amounts of silver and polymer vehicle on the two sides of the support can be the same or different. These amounts refer to dry weights.

[0049] The radiographic films generally include a surface protective overcoat on each side of the support that is typically provided for physical protection of the one or more silver halide emulsion layers. 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 illustrated by 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 emulsion layers and the surface overcoats. It is quite common to locate some emulsion compatible types of protective overcoat addenda, such as anti-matte particles, in the interlayers. 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.

[0050] The protective overcoat is generally comprised of a hydrophilic colloid vehicle, chosen from among the same types disclosed above in connection with the emulsion layers. In conventional radiographic films protective overcoats are provided to perform two basic functions. They provide a layer between the emulsion layers and the surface of the element for physical protection of the emulsion layer during handling and processing. Secondly, they provide a convenient location for the placement of addenda, particularly those that are intended to modify the physical properties of the radiographic film. The protective overcoats of the films of this invention can perform both these basic functions.

[0051] This invention in a preferred form features a light-sensitive radiographic film coated on a polyethylene terephthalate (PET) support containing a blue-tinting anthraquinone dye at a level sufficient to achieve the desired L* and b* values. In addition as an alternative to dye addition to the support, a blue tinting dye can be added to any other adjacent layers as well. The films employed with these levels of blue-tinting dyes can be used for any black-and-white photographic film application, including but not limited to medical radiography, such as mammography, dental or general-purpose radiography, and non-destructive testing e.g. industrial X-ray.

[0052] Any suitable blue dye may be utilized in the invention. Typically such dyes are anthraquinone dyes. Preferred dyes comprises:



where each of G1, G2, and G3 is independently hydrogen or any alkyl group.

[0053] Four specific preferred dyes are as follows:

Specific Blue Dye	G1	G2	G3

(continued)

Specific Blue Dye	G1	G2	G3
Dye 1	Me	Et	H
Dye 2	Et	Et	H
Dye 3	Et	Et	Me
Dye 4	Me	Me	Me

[0054] In a preferred form of the invention, radiographic film is coated on a polyethylene terephthalate support containing one or more anthraquinone blue dyes represented by the general formula above. These dyes can be added to the support and/or other adjacent hydrophilic layers. The dyes are added to the film at a level sufficient to enhance the scotopic response of the human eye. Films employed with these levels of blue-tinting dyes can be used for any black-and-white photographic film application, including but not limited to medical radiography, such as mammography, dental or general-purpose radiography, and non-destructive testing e.g. industrial X-ray.

[0055] As was stated above, radiographic films have been coated on blue-tinted film supports for many decades. During that time however there was little understanding as to why blue-tinting dyes were used other than by empirical observations. Recent understanding in the field of lighting (see reference above by Dr. S. Berman) provides greater insight to the effect of blue-tinting dyes in medical radiography. In this work, Dr. Berman states that enhancing the scotopic content of the illuminant hitting the retina of the eye leads to improvements in visualization of achromatic (black and white) tasks result. Figure 1 shows a transmittance spectrum of a blue-tinted X-ray support and it shows that the blue dye used absorbs light in the green-red region of the visible spectrum and transmits blue light. As shown in Figure 2, the color sensitivity of the rods (scotopic vision) of the eye has its peak sensitivity to blue light. We have discovered that by increasing the amount of blue dye in the radiographic film, improvements in visual response of the eye results by enhancing the scotopic content of the light reaching the eye in the viewing of an X-ray film radiograph. Surprisingly, we have found that improvements in image quality result at dye levels significantly higher than has been taught in the patent field of X-ray radiography. In addition, these levels of dyes result in film Dmin values greater than the current acceptance criteria in the standards set by various regulatory agencies. Counter to the teachings in the patent literature and as established by radiographic standards, surprisingly we have found that image quality is actually increased at these higher dye levels and subsequent film Dmin values.

[0056] The X-ray film of the inventive application can be employed in mammographic films. Dense breasts are more X-ray absorbent and present at lower film densities where blue support is more predominant. Increased visualization due from psychovisual contrast will image dense breast parenchyma better. The overall visual contrast is also increased.

[0057] The term "image quality" is a subjective factor that rates the capability of obtaining radiographically significant information in fully-processed film. The term "contrast" as herein employed indicates the average contrast derived from a characteristic curve of a radiographic film using as a first reference point (1) a density (D1) of 0.25 above minimum density and as a second reference point (2) a density (D2) of 2.0 above minimum density, where contrast is $AD (i.e. 1.75) + A \log_{10} E (\log_{10} E_2 - \log_{10} E_1)$, E1 and E2 being the exposure levels at the reference points (1) and (2).

[0058] The term "fully forehardened" is employed to indicate the forehardening of hydrophilic colloid layers to a level that limits the weight gain of a radiographic film to less than 120% of its original (dry) weight in the course of wet processing. The weight gain is almost entirely attributable to the ingestion of water during such processing. The term "rapid access processing" is employed to indicate dry-to-dry processing of a radiographic film in 45 seconds or less. That is, 45 seconds or less elapse from the time a dry imagewise exposed radiographic film enters a wet processor until it emerges as a dry fully processed film. 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. 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 of grain ECD divided by the mean grain ECD. The term "covering power" is used to indicate 100 times the ratio of maximum density to developed silver measured in mg/dm². The term "dual-coated" 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 used in the present invention are "dual-coated."

[0059] "Photographic speed" for the radiographic films refers to the exposure necessary to obtain a density of at least 1.0 plus Dmin.

[0060] The terms "warmer" and "colder" in referring to image tone are used to mean CIELAB b* values measured at minimum density, or at density = 1.2, that are more positive or negative, respectively. The b* values describe the yellowness vs. blueness of an image with more positive values indicating a tendency toward greater yellowness, a* values compare greenness vs. redness, where more positive values indicating a higher proportion toward redness. L*

or luminosity is a measure of how much light is transmitted from an object to the eye. L^* , a^* and b^* measurement techniques are described by Billmeyer and Saltzman, Principles of Color Technology, 2nd. Ed., Wiley, New York, 1981, at Chapter 3. The measurements of a^* and b^* were developed by the Commission Internationale de L'Esclairage (International Commission on Illumination).

[0061] The term "PAI" stands for the "primary active ingredient" in a material.

[0062] X-ray films have traditionally been coated on different dye-tinted film supports depending on the need for different image tone correction and / or concerns about film Dmin. As noted in the Background section, above, a portion of a film's Dmin is derived from the optical density of the film support. As can be seen, film-support Dmin has inverse relationships with both L^* and b^* as increased Dmin levels are correlated with lower L^* or b^* values. Figures 3 and 4 shows the relationships between L^* , b^* and Dmin for several commercially available X-ray film supports.

[0063] While the invention is being described with regard to radiography, those skilled in the art will recognize that the invention can be applied to other imaging applications, for example, business imaging such as document scanning.

EXAMPLES

[0064] Samples of the films were exposed through a graduated density step tablet to a MacBeth sensitometer for 0.5 second to a 500-watt General Electric DMX projector lamp that was calibrated to 2650°K filtered with a Coming C4010 filter to simulate a green-emitting X-ray screen exposure. The film samples were then processed using a processor commercially available under the trademark KODAK RP X-OMAT™ film Processor M6A-N, M6B, or M35A. Development was carried out using the following black-and-white developing composition:

Black-and-White Developing Composition	
Hydroquinone	30 g
Phenidone	1.5 g
Potassium hydroxide	21 g
pH	10
Temperature	65C

[0065] The film samples were processed for less than 90 seconds. Fixing was carried out using KODAK RP X-OMAT®LO Fixer and Replenisher fixing composition (Eastman Kodak Company). 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 D vs. logE curve was plotted for each radiographic film that was imaged and processed. Speed was measured at a density of $1.0 + D_{min}$. Gamma is the slope (derivative) of the noted curves.

[0066] Image quality was established using a detailed test object (DTO) and imaging such test object onto the film. A subjective measurement of image quality includes image sharpness, as measured on a scale of 1 to 10 (with 10 being the highest sharpness). Image sharpness is one part of image quality. Contrast and modulation-transfer function (MTF) both contribute to image sharpness.

[0067] The description below is the formation of Element A of Table 1.

Coating Diagram of Mammographic films:

[0068]

Overcoat layer 1
Interlayer
Emulsion Layer 1
Support 0.763 mg/dm ² Dye 1

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(continued)

Emulsion layer 2
Dye layer 1
Interlayer
<u>Overcoat layer 2</u>

Over coat layer 1

[0069]

Material	mg PAI/dm ²
Gelatin	2.999
polymethylmethacrylate beads	0.4516
carboxymethylcasein	0.9426
colloidal silica	0.6779
polyacrylamide	1.343
chrome alum	0.03318
Resorcinol	0.07312
sodium hydroxide	0.02827
Dow Coming lubricant DC-200	0.07988
trifluoromethanesulfonic acid, lithium salt	0.4293
Zonyl FSN	0.1846

Interlayer 1

[0070]

Material	mg PAI/dm ²
gelatin	3.601
carboxymethylcasein	0.9426
colloidal silica	0.6768
chrome alum	0.03180
resorcinol	0.07312

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(continued)

Material	mg PAI/dm ²
	0.1468
(1,2,4)Triazolo(1,5-a)pyrimidin-7-ol, 5-methyl-, sodium salt	0.5786
AWNa polymer	0.08064

Emulsion layer 1

[0071]

Material	mg PAI/dm ²
gelatin	15.13
cubic AgX emulsion	27.41
(1,2,4)Triazolo(1,5-a)pyrimidin-7-ol, 5-methyl-, sodium salt	0.3043
	1.817
3,6-Pyridazinedione, 1,2-dihydro-	0.006667
1,3-Benzenedisulfonic acid, 4,5-dihydroxy-, disodium salt	0.3861
1,2,3-Propanetriol	0.1635
potassium bromide	0.1272
1,3-Benzenediol	2.294

Support

[0072] The support is a blue-tinted PET support 170 um in thickness. The support contains 0.763 mg/dm² Dye 1.

Dye Layer

[0073]

Material	mg PAI/dm ²
gelatin	8.073
1,4-Benzenedisulfonic acid, 2-(3-acetyl-4-(5-(3-acetyl-1-(2,5-disulfophenyl)-1,5-dihydro-5-oxo-4H-pyrazol-4-ylidene)-1,3-pentadienyl)-5-hydroxy-1H-pyrazol-1-yl)-, pentasodium salt	0.1455
1H-Pyrazole-3-carboxylic acid, 1-(4-carboxyphenyl)-4-((4-(dimethylamino)phenyl)methylene)-4,5-dihydro-5-oxo-, 3-ethyl ester	2.153

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Interlayer 2

[0074]

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10

15

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Material	mg PAI/dm ²
gelatin	3.600
carboxymethylcasein	0.9426
colloidal silica	0.6768
chrome alum	0.03180
1,2,3-Propanetriol	0.07312
(1,2,4)Triazolo(1,5-a)pyrimidin-7-ol, 5-methyl-, sodium salt	0.5786
Oxiranemethanol, polymer with nonylphenol	0.3634
AWNa polymer	0.1490

Overcoat 2

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[0075]

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Material	mg PAI/dm ²
gelatin	3.320
polystyrene matte beads	0.1792
carboxymethylcasein	0.9426
	0.6779
LUDOX-AM (COLLOIDAL SILICA MODIFIED WITH ALUMINA) /DUPONT/	1.343
chrome alum	0.03180
1,3-Benzenediol	0.07312
DC-200 (POLYDIMETHYL-SILOXANE 200-CS) /DOW CORNING/	0.07988
Methanesulfonic acid, trifluoro-, lithium salt	0.4293
Zonyl FSN	0.1846

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[0076] Table 1 shows the comparative examples of Control Elements A, E-G and Inventive Elements B-D.

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Example 1- Table 1								
Element		Dye Level	Fogged Ag	Dmin	Image Tone	Speed	Contrast	Image Quality
		(mg/ dm ²)	(mg/ dm ²)					
A	Control	0		0.227	-8.7	425	4.3	5

(continued)

Example 1- Table 1								
Element		Dye Level	Fogged Ag	Dmin	Image Tone	Speed	Contrast	Image Quality
B	Invention	0.054		0.24	-9.5	424	4.3	6
C	Invention	0.11		0.258	-10.9	425	4.3	8
D	Invention	0.22		0.285	-13.1	424	4.3	9
E	Control		0.54	0.261	-8.8	424	4.3	5
F	Control		1.08	0.295	-8.6	424	4.3	5
G	Control		2.15	0.36	-8.5	424	4.2	4

[0077] Dye level is the amount of Dye 1 added to the film (mg/dm²) B, C, and D in addition to the amount of dye already in the support.

[0078] Fogged Ag is the amount of silver halide emulsion that was prefogged in Controls E, F, and G by exposing the emulsion to light for 3 minutes prior to adding to the coating melt.

[0079] Image tone is a CIELAB measurement of b* measured for the film exposed to a density of 1.0.

[0080] Dmin is the minimum density of an exposed strip of film

[0081] Speed and Contrast are measurements as described earlier in this document.

[0082] Image quality is a subjective measurement of image sharpness as described earlier. The Table 1 table shows improved image quality with the addition of more dye even at higher Dmin.

[0083] Example 1 shows the results from a coating of films intended for mammography. These films were coated on PET support containing 0.763 mg/dm² of blue dye (1) and having a L* value of 83.0 and a b* value of -19.6. Element A (Control) has a Dmin of 0.227 and reasonable image quality. Elements B-D (Inventions) have Dmin values that approach or exceed the Dmin value of 0.25 which is the limiting value established by several standards committees for mammography. Despite these values for Dmin, image tone is improved (b* more negative) and image quality is improved (higher subjective ranking). Elements EG have Dmin values that exceed the standards limits but image tone and image quality are not improved. In fact, at the highest Dmin level (Element G), image tone and image quality is slightly degraded.

Coating Diagram for Example 2 for Element A in Table 2

[0084]

Overcoat layer 1
Interlayer 1
Emulsion Layer 1
Support 0.694 mg Dye 1 /dm ²
Emulsion layer 2
Interlayer
Overcoat layer 2

Overcoat layer 1

[0085]

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Material	mg PAI/dm ²
gelatin	2.541
4 micron methylmethacrylate matte beads	0.2750
carboxymethylcasein	0.7515
polyacrylamide	0.53955
dextran	1.070
chrome alum	0.02537
1,3-Benzenediol	0.05847
DC-200 (POLYDIMETHYL-SILOXANE 200-CS) /DOW CORNING	0.06368
Methanesulfonic acid, trifluoro-, lithium salt	0.3794
Zonyl FSN	0.1475

Interlayer 1

[0086]

Material	mg PAI/dm ²
gelatin	3.600
carboxymethylcasein	0.9426
colloidal silica	0.6768
chrome alum	0.03180
resorcinol	0.07312 0.1468
(1,2,4)Triazolo(1,5-a)pyrimidin-7-ol, 5-methyl-, sodium salt	0.5786
AWNa polymer	0.08064

Emulsion layer 1

[0087]

Material	mg PAI/dm ²
gelatin	20.76
tabular grain emulsion	11.30
disulfocatechol	0.09179

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(continued)

Material	mg PAI/dm ²
3,6-Pyridazinedione, 1,2-dihydro-	0.004603
D-Glucitol	0.2819
1,2,3-Propanetriol	0.3500
1,3-Benzenediol	0.4576
polyacrylamide	2.153
Versa TL-502	0.3014

Support

[0088] The support is a blue-tinted PET support 170 um in thickness. The support contains 0.694 mg/dm² Dye 1.

Emulsion layer 2

[0089]

Material	mg PAI/dm ²
gelatin	20.76
tabular grain emulsion	11.30
disulfocatechol	0.09179
3,6-Pyridazinedione, 1,2-dihydro-	0.004603
D-Glucitol	0.2820
1,2,3-Propanetriol	0.3500
1,3-Benzenediol	0.4576
polyacrylamide	2.153
Versa TL-502	0.3014

Interlayer 2

[0090]

Material	mg PAI/dm ²
gelatin	2.803
0.08 um AgI	0.1076
carboxymethylcasein	0.7529
polyacrylamide	0.5395
dextran	1.070
chrome alum	0.02537
1,3-Benzenediol	0.05847

(continued)

Material	mg PAI/dm ²
sodium hydroxide	0.009341
5-nitroindazole	0.03778
(1,2,4)Triazolo(1,5-a)pyrimidin-7-ol, 5-methyl-, sodium salt	0.4613
Oxiranemethanol, polymer with	
nonylphenol	0.4602

Overcoat layer 2**[0091]**

Material	mg PAI/dm ²
Gelatin	1.626
4 micron methylmethacrylate matte beads	0.2750
carboxymethylcasein	0.7515
polyacrylamide	0.5395
dextran	1.070
chrome alum	0.02537
resorcinol	0.05847
DC-200 (POLYDIMETHYL-SILOXANE 200-CS) /DOW CORNING	0.06368
Siloxanes and Silicones, di-Me, 3-hydroxypropyl group-terminated, ethoxylated	0.9155
Oxiranemethanol, polymer with nonylphenol	0.9153
Methanesulfonic acid, trifluoro-, lithium salt	0.3794

[0092] The following Table 2 shows the comparative examples of Control Elements A,E-H and Inventive Elements B-D.

Example 2 - Table 2								
Element		Dye Level	Fogged Ag	Dmin	Image Tone	Speed	Contrast	Image Quality
		(mg/ dm ²)	(mg/ dm ²)					
A	Control	0		0.21	-7.8	461	2.99	5
B	Invention	0.054		0.28	-8.9	459	2.94	6
C	Invention	0.11		0.249	-10.4	458	2.95	8
D	Invention	0.22		0.279	-12.9	458	2.93	10
E	Control		0.22	0.354	-7.8	459	2.89	4
F	Control		0.54	0.493	-7.7	456	2.66	3

(continued)

Example 2 - Table 2								
Element		Dye Level	Fogged Ag	Dmin	Image Tone	Speed	Contrast	Image Quality
G	Control		1.08	0.79	-7.6	452	2.3	2
H	Control		1.61	0.911	-7.2	449	1.8	1

[0093] Dye level is the amount of Dye 1 added to the film (mg/dm²) in addition to the amount of dye already in the support. The additional dye was split between the emulsion layers.

[0094] Fogged Ag is the amount of silver halide emulsion that was prefogged by exposing the emulsion to light for 3 minutes prior to adding to the coating melt.

[0095] Image tone is a CIELAB measurement of b* measured for the film exposed to a density of 1.0.

[0096] Dmin is the minimum density of an exposed strip of film.

[0097] Speed and Contrast are measurements as described earlier in this document.

[0098] Image quality is a subjective measurement of image sharpness as described earlier.

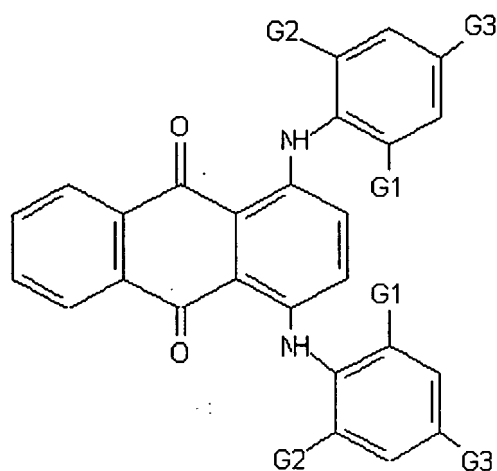
[0099] Example 2 - Table 2 shows the results from a coating of films intended for general-purpose radiography. These films were coated on blue-tinted PET support containing 0.694 mg/dm² blue dye of the type described above and having a L* value of 84.8 and a b* value of -17.1. Element A (Control) has a Dmin of 0.21 and reasonable image quality. Elements B-D (Inventions) have Dmin values that approach the Dmin value of 0.30 which is the limiting value established by several standards committees for general purpose radiography. Despite these values for Dmin, image tone is improved (b* more negative) and image quality is improved (higher subjective ranking). Elements E-G have Dmin values that exceed the standards limits but image tone and image quality are not improved. In fact, image tone and image quality is significantly degraded for all of the radiographic elements (E-G) with the highest Dmin levels.

[0100] The invention has been described in detail with particular reference to a presently preferred embodiment, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention. The presently disclosed embodiments are therefore considered in all respects to be illustrative and not restrictive. The scope of the invention is indicated by the appended claims, and all changes that come within the meaning and range of equivalents thereof are intended to be embraced therein.

Claims

1. An imaging element comprising a polymer support, a blue dye sufficient to result in a CIELAB measurement of L* less than or equal to 80 and a b* less than or equal to -25.
2. The imaging element of claim 1 wherein the blue dye comprises an anthraquinone.
3. The imaging element of claim 1 wherein L* is between 70 and 80.
4. The imaging element of claim 1 wherein b* is between -25 and -35.
5. The imaging element of claim 1 wherein the imaging element comprises silver halide.
6. The imaging element of claim 5 wherein the silver halide comprises silver bromiodide.
7. The imaging element of claim 5 wherein the silver halide comprises a tabular silver halide.
8. The imaging element of claim 5 wherein the silver halide comprises monodisperse cubic silver halide.
9. The imaging element of claim 5 wherein the silver halide is comprised of a halide composition having any combination of bromide, iodide, and chloride, subject to the sum total of halide moles equal to the moles of silver.
10. The imaging element of claim 1 further comprising an emulsion layer, wherein the blue dye is in the emulsion layer.
11. The imaging element of claim 1 wherein the blue dye is in the polymer support.

12. The imaging element of claim 1 wherein the blue dye comprises:

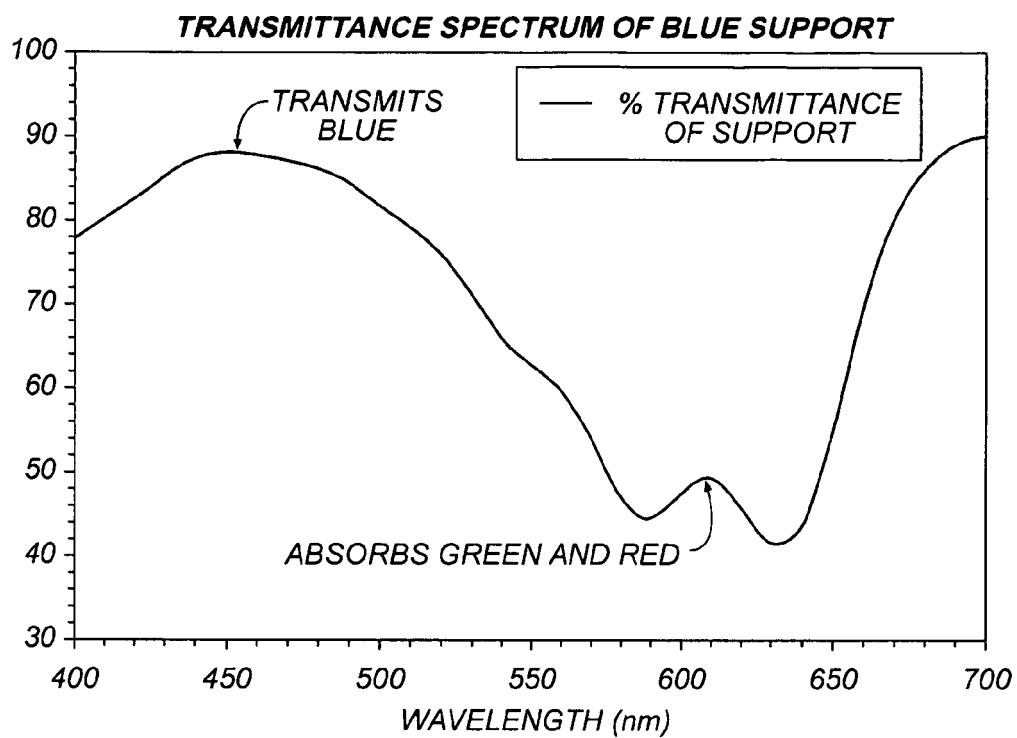


where each of G1, G2, and G3 is hydrogen or any alkyl group.

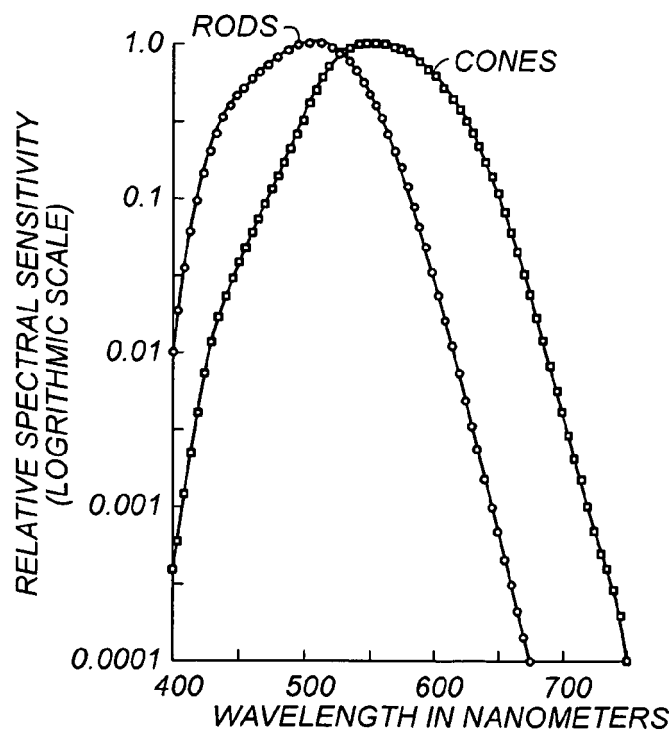
13. The imaging element of claim 1 wherein the polymer support comprises a polyethylene terephthalate.

14. The imaging element of claim 1 wherein the blue dye is in at least one emulsion layer and in the polymer support.

15. The imaging element of claim 1 wherein the imaging element is a radiographic element.



SPECTRAL SENSITIVITY OF THE RODS AND CONES OF THE EYE



OPTICAL CHARACTERISTICS OF COMMERCIALY-AVAILABLE FILM SUPPORTS

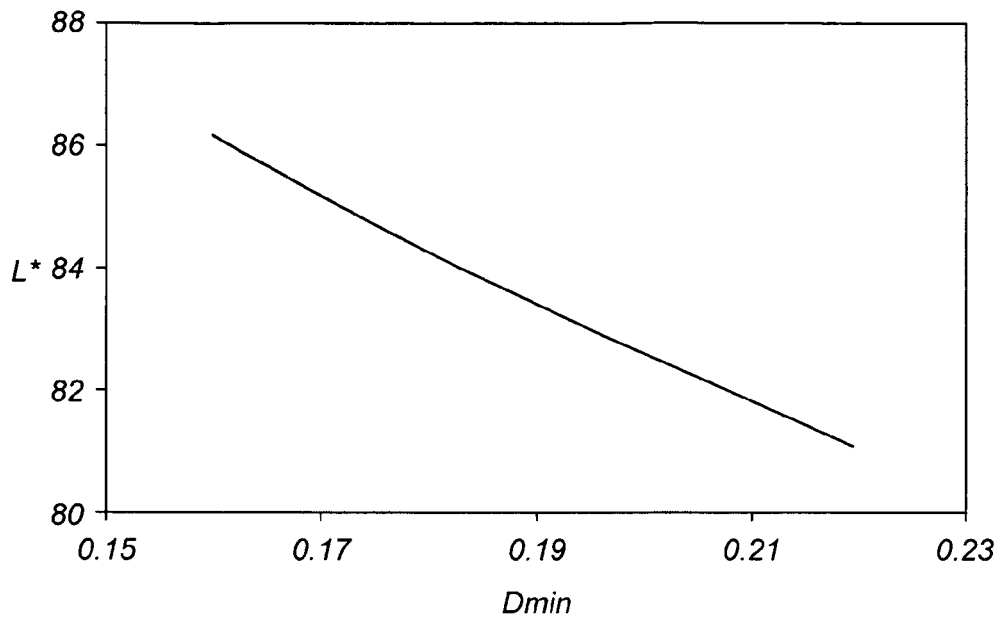


FIG. 3

OPTICAL CHARACTERISTICS OF COMMERCIALY-AVAILABLE FILM SUPPORTS

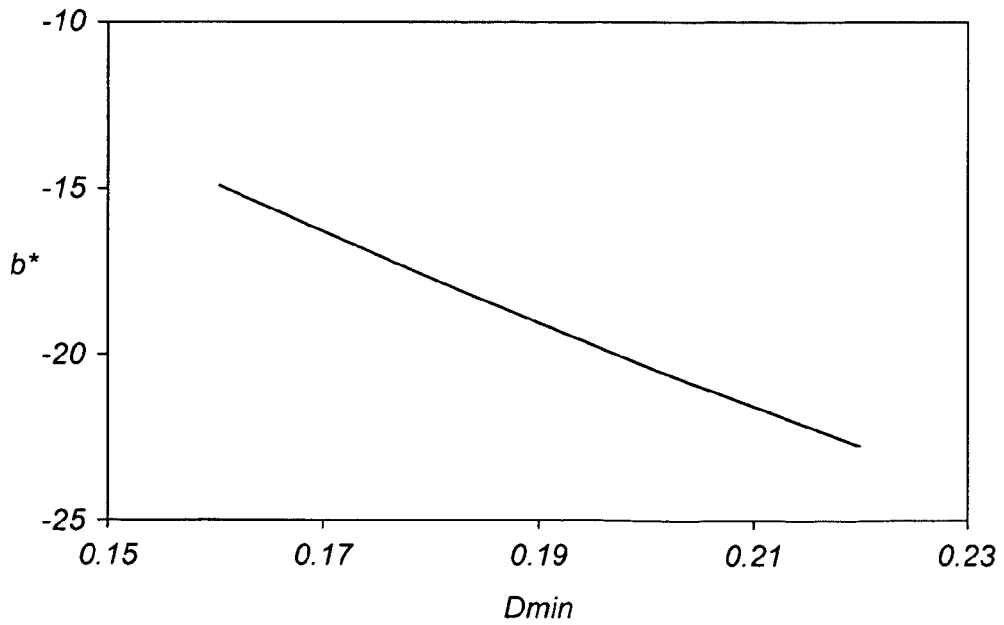


FIG. 4



EUROPEAN SEARCH REPORT

Application Number
EP 10 00 3593

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The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 23 April 2010	Examiner Magrizo, Simeon
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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EUROPEAN SEARCH REPORT

Application Number
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The Hague		23 April 2010	Magrizo, Simeon
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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23-04-2010

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