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(54) Improved dye imbibition printing blanks and matrix films

(57) Dye imbibition printing blanks are disclosed comprising a support bearing on one side thereof a dye-receiving layer comprising a cationic mordant, and further comprising an antistat layer substantially free of cationic polymers. The antistatic layer is preferably provided on the opposite side of the support relative to the dye-receiving layer. Such antistatic layer provides improved antistatic properties which enable high manufacturing and processing speeds without adversely affecting printed image qualities. In a preferred embodiment, the dye receiving layer comprises a cationic mordant, a hydrophilic colloid and a plasticizer polymer, wherein the plasticizer polymer is a latex polymer having a glass transition temperature below about 30°C comprising from about 2 to 20 wt% of units having a quaternary ammonium group. Use of such latexes provide dye imbibition printing blanks substantially free of haze and brittleness. A process for exposing dye imbibition printing matrix films is also disclosed comprising imagewise exposing a matrix film comprising a visible light sensitive silver halide emulsion containing colloid layer on a support to blue, green or red light, wherein the visible light sensitive emulsion is also sensitive to UV light and the toe contrast of the imaged matrix film is controlled by (i) incorporating a UV absorber in the colloid layer of the matrix film, and (ii) flash exposing the matrix film with UV light in the substantial absence of light having a wavelength above 410 nm, wherein the UV absorber provides sufficiently low absorption above 410 nm such that it does not substantially alter the effective photographic speed of the matrix film during the imagewise exposure or the mid scale contrast of the imaged matrix film, and sufficiently high absorption to the UV light to decrease the resulting toe contrast of the imaged matrix film.

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Description

Field of the Invention

This invention relates to a photographic imbibition dye transfer process and imbibition printing materials. It relates particularly to improved dye imbibition printing blanks with improved antistatic properties and reduced haze, improved imbibition printing matrix films, and use of such materials in forming an imbibition print.

Background of the Invention

The imbibition printing dye transfer process is well known. According to common procedures, a tanned colloid relief image is formed by imagewise exposure of a suitable light sensitive layer on a support, differentially hardening the colloid layer in accordance with the imagewise exposure, and removing the colloid from the support in inverse proportion to the amount of imagewise light exposure. The differential colloid hardening and removal is conventionally performed with a pyrogallol hardening developer as described, e.g., in U.S. Patent 2,837,430. For full color prints, three separate relief images corresponding to the blue, green, and red color records of the image being reproduced may be formed in separate blue, green, and red light sensitive matrix films by three separate exposures though a color negative film. The resultant colloid relief images are then dyed with yellow, magenta and cyan dyes, and the dye images transferred to an imbibition printing blank receiver film. In this manner imbibition printed colored dye images may be obtained which faithfully reproduce a colored subject. Imbibition printing blanks typically comprise a dye receiving layer on a support. Where the resulting image is intended to be viewed by light projection, such as in a motion picture film, a transparent film support is generally used.

The photographic industry has long recognized the need to provide photographic film and paper with antistatic protection to prevent the accumulation of static charges during manufacture and use. Such protection is advantageous in photographic elements as static charges can cause irregular fog patterns in photographic silver halide imaging emulsions. To prevent the problems arising from an accumulation of static charges, it is conventional practice to provide an antistatic layer (i.e., a conductive layer) in a photographic element.

A wide variety of antistatic layers are known for use in photographic elements. Such layers, however, have not previously been used with dye imbibibition printing blanks. As the visual dye image is transfered to an imbibition printing element blank rather than being formed directly in a silver halide emulsion imaging layer of the element, and as the back side of an imbibition printing element support bearing a dye receiving layer will be in contact with such dye receiving layer when the element is rolled up, such printing elements have different requirements as to antistatic protection needs. While image fog problems due to static charge buildup are generally not a problem with imbibition printing elements, such charges may attract dirt and dust to the printing element surface under high manufacturing and processing speeds which may result in the formation of "pinholes" in the processed imbibition printing blanks as well as a variety of handling and conveyance problems.

U.S. Patents 3,625,694; 3,958,995; and 3,898,088 disclose cationic (basic) mordants which may be used in dye imbibition printing blanks. Such mordants are suitable for use with anionic (acid) printing dyes. When using blanks containing a dye receiving layer comprising a cationic mordant and a hydrophilic colloid such as gelatin as a binder, there is a tendency for the blank to be brittle resulting in cracking and degradation of the transferred dye image.

The necessity for maintaining flexibility in film is obvious in view of the handling to which it is subjected in manufacturing and use. For example, films are flexed and bent during use in cameras, printers, projectors, and processing equipment. The brittleness of film is affected by both temperature and relative humidity, the latter being generally of greater practical importance. Below approximately 25 percent relative humidity, a significant change in film brittleness may occur with only a small change in relative humidity. The failures in film as a result of lack of flexibility may be of different types, depending upon the nature of the stress.

It has been suggested to include plasticizers in imbibition printing blanks and photographic elements to reduce brittleness. U.S. Patents 2,882,156 and 3,709,690 disclose blanks containing mordants and polymer latices as plasticizers. U.S. Patent 5,135,835 relates to heat developable photographic elements which contain a mordant, oil droplets and a polymer latex having a glass transition temperature (Tg) of 40°C or less for improving brittleness.

The imbibition process normally results in a sensitometric Density vs. Log-Exposure curve shape with a relatively sharp (high contrast) "toe", or lower scale, region for the developed matrix films and resulting imbibition prints. The toe region is generally regarded as the curved region below the straight, or mid-scale, region of a D-LogE sensitometric curve. Reducing the toe area contrast, or "softening" the toe, is often desirable to extend the latitude of the matrix film. One process which has been used to control the toe contrast is "flashing". Flashing is the non-selective low level exposure of a photographic material with the intent of softening the toe region of the sensitometric curve. While flashing of photographic materials to control contrast is a well known procedure, imbibition printing matrix films are unique in that the light sensitive layer of the matrix film generally has a large portion of a visible light absorbing non-photosensitive

material, such as carbon particles, coated along with silver halide and colloid materials. The carbon absorbs light as it passes through the matrix film, thus concentrating the exposure towards the base (the exposure in this process is conventionally made through the base). A normal flash exposure with this type of material accordingly will not control the curve shape in the desired manner to the desired extent.

In years past, green and red matrix films having sufficient native blue sensitivity have been flashed with blue light in order to control the lower-scale sensitometry. A yellow dye was added to the matrix film which had the effect of lowering the contrast of the flash exposure. This allowed good control of the curve shape for the green and red matrix films. The blue matrix film, however, could not use the yellow dye for the flash exposure control since the main image exposure is also made with blue light which would be absorbed by the yellow dye. In years past, however, relatively coarse (larger grain size) emulsions were used which had inherently relatively low toe contrasts. The blue matrix film (very coarse grain emulsion) was low enough in contrast that a minimal blue flash was required to control toe contrast. Thus, the blue matrix film was flashed with blue light without the presence of a yellow dye.

For blue matrix films made with modern fine grained emulsions, however, which are inherently relatively higher in contrast, blue flash toe contrast control is not effective. Additionally, when using green and red matrix films containing excess yellow absorber dye, there is a tendency for the film to become very brittle resulting in cracking and degradation of the dye image, as well as dirt generation in manufacture and use of the film. While the lower inherent contrast of previously used coarser emulsions required only relatively low levels of yellow absorber dye in the green and red matrix films for sufficient toe contrast control, modern fine grain emulsions used in green and red matrix films are also inherently relatively higher in contrast and much larger quantities of the yellow absorber dye is needed to control the toe contrast. This can lead to physical problems such as tackiness, brittleness and film fracturing in manufacture of the film.

Problems to be Solved

It would be desirable to improve the manufacturability of dye imbibition printing material and the image quality of imbibition prints.

Accordingly, it would be desireable to provide cationic mordanted imbibition printing element blanks with sufficient antistatic properties which enable high manufacturing and processing speeds without adversely affecting printed image qualities.

Additionally, often when polymer latices are added to a mordant layer containing a cationic mordant the layer becomes hazy due to incompatibility between the latex and the mordant. It would accordingly be further desirable to provide a polymeric plasticizer for use with cationic mordants which would not result in increased haze.

It would also be desirable to provide effective toe contrast control for each of the blue, green and red imbibition printing matrix films without physical problems such as tackiness, brittleness and film fracturing in manufacture of the film, and especially to provide such control in a consistent manner.

Summary of the Invention

In one embodiment, this invention provides an improved dye imbibition printing blank comprising a support bearing on one side thereof a dye-receiving layer comprising a cationic mordant, and further comprising an antistatic layer substantially free of cationic polymers. In a preferred embodiment of the invention, the antistatic layer is provided on the opposite side of the support relative to the dye-receiving layer. Such antistatic layer provides improved antistatic properties which enable high manufacturing and processing speeds without adversely affecting printed image qualities.

In a further embodiment of the invention, printing blanks are provided wherein the dye-receiving layer comprises a cationic mordant, a hydrophilic colloid and a plasticizer polymer, wherein the plasticizer polymer is a latex polymer having a glass transition temperature below about 30°C comprising from about 2 to 20 wt% of units having a quaternary ammonium group. In a preferred embodiment, the latex polymer comprises a vinyl co-polymer addition product of from about 50 to 98 weight percent of acrylic or methacrylic ester units, 0 to 48 weight percent of vinyl benzene units and 2 to 20 weight percent of the quaternary ammonium group containing unit. Use of such latex provides a dye imbibition printing blank substantially free of haze and brittleness.

In another embodiment of the invention, a UV (Ultra Violet) absorber dye is incorporated in a dye imbibition printing matrix film, and preferably in each of the blue, green and red matrix films, to attenuate light in the UV region, which for the purposes of this invention is defined as less than 400 nm. Preferably, the spectral characteristics of the UV absorber do not interfere with the main imagewise exposure of the matrix films. In accordance with such embodiment of the invention, a process for exposing dye imbibition printing matrix films is disclosed comprising imagewise exposing a matrix film comprising a visible light sensitive silver halide emulsion containing colloid layer on a support to blue, green or red light, wherein the visible light sensitive emulsion is also sensitive to UV light and the toe contrast of the imaged matrix film is controlled by (i) incorporating a UV absorber in the colloid layer of the matrix film, and (ii) flash exposing the matrix film with UV light in the substantial absence of light having a wavelength above 410 nm, wherein the UV

absorber provides sufficiently low absorption above 410 nm such that it does not substantially alter the effective photographic speed of the matrix film during the imagewise exposure or the mid scale contrast of the imaged matrix film, and sufficiently high absorption to the UV light to decrease the resulting toe contrast of the imaged matrix film. In accordance with preferred embodiments of the invention, the above contrast control process is performed for each of the blue, green and red matrix films to be used in an imbibition printing process, wherein each matrix comprises a blue, green or red light sensitive silver halide emulsion which is additionally sensitive to UV light.

In accordance with another embodiment of the invention, a matrix film for use in imbibition printing is disclosed comprising a support bearing a colloid layer comprising (i) a visible light sensitive silver halide emulsion which is also sensitive to UV light, (ii) visible light absorbing non-photosensitive particles, (iii) a hydrophilic colloid, and (iv) a UV absorber having a peak absorbance between 360 and 410 nm. Use of matrix films in accordance with the invention achieves desired toe contrast control of all three matrix films in the same manner. The blue matrix film no longer requires to be treated differently. This allows use of identical matrix films having blue, green and red sensitivity (e.g., a panchromatic sensitive film) in forming the separate blue, green and red exposed relief images if desired. The invention also allows greater control over matching the sensitometric contrast curves of the three matrix films. Additionally, preferred UV absorber dyes absorb UV light more efficiently than the yellow dye previously used in green and red matrix films absorbed blue light such that much less dye is needed to attain a specific density, which results in good physical characteristics of the matrix films.

In further embodiments of the invention, imbibition prints are formed by registration printing yellow, magenta and cyan dye images formed in matrix films exposed as described above onto printing blanks as described above.

Brief Description of the Drawings

Figure 1 depicts the absorption spectrum of a preferred UV absorbing dye.

Figure 2 depicts the spectral characteristics of a HOYA U-340 filter.

Figure 3 is a graph depicting the Matrix Exposure Profile for matrix films having various UV dye optical densities.

Figure 4 depicts the sensitometric curves for matrix films having varying levels of UV absorber dye exposed to UV light resulting from Example 4.

Figure 5 is a graph depicting the Best Fit Contrasts of the curves of Figure 4 vs. UV dye concentration.

Figure 6 depicts the absorption spectra of the UV absorbing dyes used in Example 5.

Figure 7 depicts the sensitometric curves for the matrix films exposed to UV light resulting from Example 5.

Detailed Description of the Invention

Dye imbibition printing blanks within the scope of one embodiment of this invention comprise a support bearing on one side thereof a dye receiving layer containing a cationic mordant, and further comprise an antistatic layer. In a preferred embodiment, in addition to the cationic mordant, the dye image receiving layer also comprises a hydrophilic colloid, and a plasticizer polymer.

Any antistatic conductive materials, excluding cationic polymers, such as those previously suggested for use with photographic elements may be used in the printing element antistatic layer in accordance with the invention. Such materials include, e.g., anionic polymers, electronic conducting non-ionic polymers, and electrically-conductive metal-containing particles such as metal halides or metal oxides in polymer binders. While antistatic compositions comprising a cationic polymer are also applicable for use with conventional photographic elements, such as the highly crosslinked vinylbenzyl quaternary ammonium polymer disclosed in U.S. Patent 4,070,189, such antistatic materials are excluded from the scope of the instant invention. Dyes intended for printing on the cationic mordant containing printing blanks of the invention are anionic and will transfer from the front dye-receiving side of the film to the antistat backing when such sides come into contact (such as in a rolled film) if the backing contains a catonic polymeric material such as quaternary ammonium polymer, resulting in dye stain. For the purposes of this invention, "substantially free of cationic polymers" is intended to apply to the absence of cationic polymers above trace or impurity levels.

Examples of suitable antistatic materials and layers include the following. U.S. Patent 3,033,679 discloses an antistatic layer comprised of an alkali metal salt of a copolymer of styrene and styrylundecanoic acid. Films having a metal halide, such a sodium chloride or potassium chloride, as the conducting material in a hardened polyvinyl alcohol binder are described in U.S. Patent 3,437,484. In U.S. Patent 3,525,621, the antistatic layer is comprised of colloidal silica and an organic antistatic agent such as an alkali metal salt of an alkylaryl polyether sulfonate, an alkali metal salt of an arylsulfonic acid, or an alkali metal salt of a polymeric carboxylic acid. An antistatic layer comprised of an anionic film forming polyelectrolyte, colloidal silica, and a polyalkylene oxide is disclosed in U.S. Patent 3,630,740 while U.S. Patent 3,681,070 describes a copolymer of styrene and styrene sulfonic acid as an antistatic agent. U.S. Patent 4,542,095 describes antistatic compositions comprising a binder, a nonionic surface-active polymer having polymerized alkylene oxide monomers, and an alkali metal salt. In U.S. Patent 4,916,011, an antistatic layer comprising a styrene

sulfonate-maleic acid copolymer, a latex binder, and an alkyl-substituted trifunctional aziridine crosslinking agent are disclosed. Antistat layers comprising a polythiophene with conjugated polymer backbone in the presence of a polymeric polyanion compound are described in EP 554,588; EP 553,502; EP 564,911; DE 4,138,628.

Any of the wide diversity of electrically-conductive metal-containing particles proposed for use heretofore in imaging elements can be used in the electrically-conductive antistatic layer of this invention. Examples of useful electrically-conductive metal-containing particles include donor-doped metal oxides, metal oxides containing oxygen deficiencies, and conductive nitrates, carbides or borides. Specific examples of particularly useful particles include conductive TiO_2, SnO_2, Al_2O_3, ZrO_2, In_2O_3, ZnO, TiB_2, ZrB_2, NbB_3, CrB_2, MoB, Wb, LaB_6, ZrN, TiN, TiC, WC, HfN, and ZrC.

Metal oxides, and particularly vanadium pentoxide as described, for example, in Guestaux, U.S. Patent 4,203,769, are preferred for use in the dye imbibition printing elements of the invention. Antistatic layers containing vanadium pentoxide provide excellent protection against static and are highly advantageous in that they have excellent transparency and their performance is not significantly affected by changes in humidity. The use of metal oxide materials is further advantageous, as their antistatic properties allow the use of a protective overcoat layer such as a layer of cellulosic material to provide abrasion protection and/or enhance frictional characteristics while still providing acceptable antistatic performance.

Conductive fine particles of crystalline metal oxides dispersed with a polymeric binder have been used to prepare optically transparent, humidity insensitive, antistatic layers for various imaging applications. Many different metal oxides, such as AnO, TiO_2, ZrO_2, Al_2O_3, SiO_2, MgO, BaO, MoO_3, and V_2O_5, are disclosed as useful as antistatic agents in photographic elements or as conductive agents in electrostatographic elements in such patents as U.S. Patents 4,275,103; 4,394,441; 4,416,963; 4,418,141; 4,431,764; 4,495,276; 4,571,361; 4,999,276; and 5,122,445, the disclosures of which are hereby incorporated by reference. Preferred metal oxides are antimony doped tin oxide, aluminum doped zinc oxide, and niobium doped titanium oxide, as these oxides have been found to provide acceptable performance characteristics in demanding environments.

Particular preferred metal oxides are antimony-doped tin oxide and vanadium pentoxide having good resistance to static discharge and no dye stain resulting from transfer of dye from front side to the back of the film. For high dye imbibition printing blank manufacturing and processing speeds (e.g., transport speeds above about 60 m/s), a surface resistivity of less than 10^9 ohms per square is desired for the printing blanks to prevent static discharges during unwinding of the film and the buildup of static dirt during handling of the film.

Preferred binders which may be included in the antistatic layer of the printing blanks of the invention include vinylidene chloride-containing latexes and polyesterionomer dispersions, which can improve the integrety of the layer and the adhesion of the layer to the support. Polyesterionomer refers to polyesters that contain at least one ionic moiety. Such ionic moieties function to make the polymer water dispersable. These polymers are prepared by reacting one or more dicarboxylic acids or their functional equivalents such as anhydrides, diesters, or diacid halides with one or more diols in melt-phase polycondensation reactions well known in the art as shown in U.S. Patents 3,018,272, 3,929,489, 4,307,174 and 4,419,437. Examples of this class of polymers include, for example, Eastman AQ polyesterionomers manufactured by Eastman Chemical Company.

To provide protection of the antistatic layer, a protective overcoat may be applied thereon. The protective layer can chemically isolate the antistatic layer and also serve to provide scratch and abrasion resistance. The protective overcoat layers may be, e.g., cellulose esters, cellulose nitrate, polyesters, acrylic and methacrylic copolymers and homopolymers, polycarbonates, polyvinyl formal polymethyl methacrylate, polysilicic acid, polyvinyl alcohol, and polyurethanes. Such layers may be aqueous coated or organic solvent coated as appropriate.

The chemical resistance of the antistatic layer or an overcoat can be improved by incorporating a polymer cross-linking agent into the antistatic layer or those overcoats that have functionally crosslinkable groups. Cross-linking agents such as aziridines, carbodiimide, epoxys, and the like are suitable for this purpose.

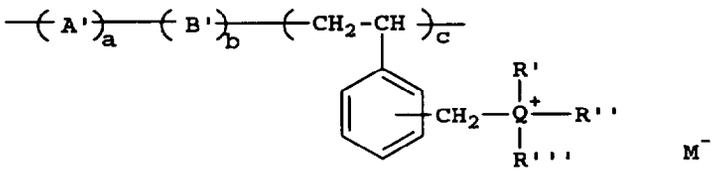
A suitable lubricant may also be included in the antistatic layer or protective overcoat in order to provide desired friction performance to assure good transport characteristics during manufacturing and handling of the elements of the invention. Many lubricating agents can be used including higher alcohol esters of fatty acids, higher fatty acid calcium salts, metal stearates, silicone compounds, paraffins and the like. Aqueous dispersed lubricants are preferred as they may be directly incorporated into an aqueous antistatis or overcoat layer, thus avoiding the need for a separately applied lubricant layer. The aqueous dispersed lubricants of carnauba wax and stearates are preferred for their effectiveness in controlling friction at low lubricant levels and their excellent compatibility with aqueous overcoat polymer solutions.

Matting agents may also be included in the antistatic layer or overcoat thereon in order to improve transport properties of the elements of the invention on manufacturing, printing, processing, and projecting equipment. Such matting agents can also help prevent sticking between the front and back sides of the elements in a tightly wound roll. Matting agents may be silica, calcium carbonate, other mineral oxides, glass speres, ground polymers and high melting point waxes, and polymeric matte beads.

The antistatic layer may also contain a coating aid to improve coatability, including anionic or nonionic coating aids

such as para-isononylphenoxyglycidol ethers, octylphenoxy polyethoxy ethanol, sodium salt of alkylaryl polyether sulfonate, and dioctyl esters of sodium sulfossuccinic acid, which coating aids are typically used at from 0.01 to 0.30 weight percent based on the total coating solution weight.

Cationic mordants for use in the dye receiving layer of the printing blanks in accordance with the invention are preferably quaternary ammonium and phosphonium mordants of the type described in U.S. Pats. 3,898,088 and 3,958,995. The cross-linked mordants of U.S. Pat. 3,958,995 are particularly preferred. Such mordants are generally of the formula:



wherein A' represents units of an addition polymerizable monomer containing at least two ethylenically unsaturated groups; B' represents units of a copolymerizable α,β-ethylenically unsaturated monomer; Q is N or P; R', R", and R"' are independently carbocyclic or alkyl groups; M^- is an anion; a is from about 0.25 to 5 mole percent, preferably from about 1 to 10 mole percent; b is from about 0 to 90 mole percent, preferably from about 0 to 60 mole percent; and c is from about 10 to 99 mole percent, preferably from about 40 to 99 mole percent, for effective dye mordanting.

It is understood throughout this specification that any reference to a substituent by the identification of a group containing a substitutable hydrogen (e.g. alkyl, amine, aryl, alkoxy, heterocyclic, etc.), unless otherwise specifically stated, shall encompass not only the substituent's unsubstituted form, but also its form substituted with any other photographically useful substituents. Typical examples of photographic substituents include alkyl, aryl, anilino, carbonamido, sulfonamido, alkylthio, arylthio, alkenyl, cycloalkyl, and further to these exemplified are halogen, cycloalkenyl, alkinyl, heterocyclyl, sulfonyl, sulfinyl, phosphonyl, acyl, carbamoyl, sulfamoyl, cyano, alkoxy, aryloxy, heterocyclyloxy, siloxy, acyloxy, carbamoyloxy, amino, alkylamino, imido, ureido, sulfamoylamino, alkoxycarbonylamino, aryloxycarbonylamino, alkoxycarbonyl, aryloxycarbonyl, heterocyclylthio, spiro compound residues and bridged hydrocarbon compound residues. Usually the substituent will have less than 30 carbon atoms and typically less than 20 carbon atoms.

The hydrophilic colloid may be any of those generally employed in the photographic field, including, for example, gelatin, colloidal albumin, polysaccharides, cellulose derivatives, water-soluble polymer or copolymer including, but not limited to polyvinyl compounds, including polyvinyl alcohol and derivatives thereof, partially hydrolyzed poly(vinylacetate-co-vinylalcohol), hydroxyethyl cellulose, poly(acrylic acid), poly(1-vinylpyrrolidone), poly(sodium styrene sulfonate), poly(2-acrylamido-2-methane sulfonic acid), polyacrylamides. Copolymers of these polymers with hydrophobic monomers may also be used. Gelatin is a preferred hydrophilic colloid. This may be gelatin per se or a modified gelatin such as acetylated gelatin, phthalated gelatin, oxidized gelatin, etc. Gelatin may be base-processed, such as lime-processed gelatin, or may be acid-processed, such as acid processed ossein gelatin.

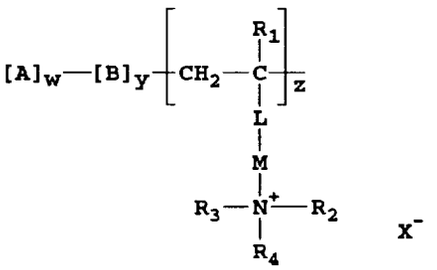
In a preferred embodiment of the invention, the dye-receiving layer of the printing blanks are hardened with a cross-linking agent. Various types of hardeners are useful in conjunction with elements of the invention. In particular, bis(vinylsulfonyl) methane, bis(vinylsulfonyl) methyl ether, 1,2-bis(vinylsulfonylacetamido) ethane, 2,4-dichloro-6-hydroxy-s-triazine, triacryloyltriazine, and pyridinium, 1-(4-morpholinylcarbonyl)-4-(2-sulfoethyl)-, inner salt are particularly useful. Also useful are so-called fast acting hardeners as disclosed in U.S. Patents 4,418,142; 4,618,573; 4,673,632; 4,863,841; 4,877,724; 5,009,990; 5,236,822.

In a preferred embodiment, the dye receiving layer of the imbibition printing blanks of the invention include a plasticizer polymer latex. Such latex polymer are preferably water insoluble vinyl copolymers derived from any copolymerizable monomers, such as α,β-ethylenically unsaturated monomer (including two, three, or more repeating units) such as ethylene, propylene, 1-butene, isobutene, 2-methylpentene, 2-methylbutene, 1,1,4,4-tetramethylbutadiene, styrene, α-methylstyrene; monoethylenically unsaturated esters of aliphatic acids such as vinyl acetate, isopropenyl acetate, allyl acetate, etc.; esters of ethyleneically unsaturated mono- or dicarboxylic acids such as methyl methacrylate, ethyl acrylate, diethyl methylenemalonate, etc.; monoethylenically unsaturated compounds such as acrylonitrile, allyl cyanide, and dienes such as butadiene and isoprene. The particular monomer units and their proportions may be selected to achieve a desired glass transition temperature for the resulting polymer as is well known in the art.

For effective plasticizing, and as a distinguishing factor from cationic dye mordants, the plasticizer polymers of the invention have a glass transition temperature of about 30°C or lower, more preferably about 20°C or lower. The latex polymers comprise from about 2 to 20 wt%, more preferably 2 to 10 wt%, of units having a quaternary ammonium group. Such units are preferably acrylic or methacrylic esters or amides to which the quaternary ammonium group is

appended. A preferred class of ethylenically unsaturated monomers which may be used to form the remaining 80 to 98 wt% portion of the preferred vinyl polymers of this invention includes acrylic or methacrylic esters and vinyl benzenes.

In preferred embodiments of the invention, the units of the plasticizer latex polymer having a quaternary ammonium group are as defined in Formula I below, and in particularly preferred embodiments of the invention the plasticizer latex is of the Formula I.



Formula I

wherein A represents units derived from an acrylic or methacrylic ester monomer; B represents units derived from a vinyl benzene monomer; R_1 is H or methyl; L is -C(O)O-, -C(O)NH-, or an aromatic linking group such as phenyl; M is a C_1 to C_{12} alkenyl linking group, which may be straight, branched, or cyclic; R_2, R_3, and R_4 are C_1 to C_6 alkyl groups; X^- is an anionic counterion such as $CH_3SO_4^-$, Cl^-, Br^-, or I^-; w is 50 to 98 weight percent; y is 0 to 48 weight percent; and z is 2 to 20 weight percent.

Representative plasticizer polymers in accordance with one embodiment of the invention include the following:

PP-1 poly(ethylacrylate-co-styrene-co-2-(N,N,N-trimethylammonium)ethyl methacrylate methosulfate) 71/19/10 wt

PP-2 poly(ethylacrylate-co-2-(N,N,N-trimethylammonium)ethyl methacrylate methosulfate) 90/10

PP-3 poly(butyl acrylate-co-styrene-co-2-(N,N,N-trimethylammonium)ethyl methacrylate methosulfate) 71/19/10 wt

PP-4 poly(methyl acrylate-co-2-(N,N,N-trimethylammonium)ethyl methacrylate methosulfate) 95/5 wt

PP-5 poly(ethyl acrylate-co-styrene-co-2-(N,N,N-trimethylammonium)ethyl methacrylate methosulfate) 75/20/5 wt

PP-6 poly(butyl acrylate-co-3-(N,N,N-trimethylammonium)propyl methacrylamide methosulfate) 90/10 wt

PP-7 poly(butyl acrylate-co-4-vinyl-N-methylpyridinium methylsulfate) 90/10 wt

PP-8 poly(butyl acrylate-co-p-N-(vinylbenzyl)-N,N,N-trimethylammonium chloride) 90/10 wt

The plasticizer polymers may be synthesized as set forth in the representative synthesis example described below or by using other well known vinyl polymer synthesis procedures.

The plasticizer polymer in accordance with the preferred embodiment of the invention must contain a quaternary ammonium group to give acceptable haze and coating solution stability. Plasticizer latices which contain anionic groups cannot be coated because the mordant layer coating composition coagulates upon the addition of latices containing an anionic group.

Matrix films for use with printing blanks in imbibition printing dye transfer processes of the invention typically comprise a support bearing a light sensitive layer containing a hydrophilic colloid (typically gelatin), visible light absorbing particles (typically carbon), a silver halide light sensitive emulsion, plus various photographic addenda to provide satisfactory stability, as well as coating aids necessary for suitable manufacture. Sensitizing dyes may be used in the matrix films to provide blue, green, and red light sensitivity for recording the blue, green, and red color record imagewise exposures. Separate matrix films designed to optimize sensitivity for particular color record exposures may be used, or alternatively identical pan-sensitive matrix films may be used for each of the blue, green and red exposures.

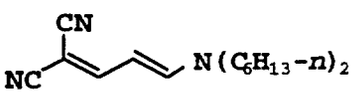
In the following discussion of suitable materials for use in the matrix film and printing blank elements of the invention, reference will be made to Research Disclosure, September 1994, Item 36544, available as described above, which

will be identified hereafter by the term "Research Disclosure." The Sections hereafter referred to are Sections of the Research Disclosure, Item 36544.

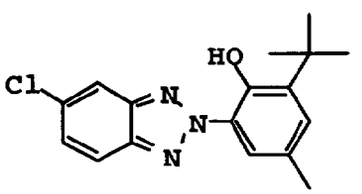
Suitable silver halide emulsions and their preparation as well as methods of chemical and spectral sensitization are described in Sections I, and III-IV. Preferred matrix film silver halide emulsions are AgBrI cubic emulsions (e.g., 1-6 mole % iodide), and have an average cubic edge length of less than 0.5 microns, more preferably less than 0.3 microns, and most preferably less than 0.25 microns. Silver halide emulsions of all types generally exhibit native sensitivity to UV light. The native UV sensitivity of the silver halide emulsion is preferably used to record the toe contrast controlling UV flash. Alternatively or additionally, sensitizing dyes and/or other components may also contribute to emulsion sensitization in the UV region.

Matrix films in accordance with the invention comprise a hydrophilic colloid or mixture of such colloids generally employed in the photographic field as described above, preferably gelatin. Vehicles and vehicle related addenda are described in Section II. Various other additives such as UV dyes, brighteners, luminescent dyes, antifoggants, stabilizers, light absorbing and scattering materials, coating aids, plasticizers, lubricants, antistats and matting agents may be included, as described, for example, in Sections VI-IX. Dye image formers and modifiers are described in Section X. Layers and layer arrangements, color negative and color positive features, scan facilitating features, supports, exposure and processing can be found in Sections XI-XX.

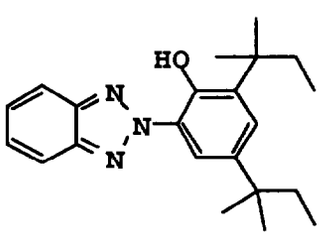
In accordance with one embodiment of the invention, a UV (Ultra Violet) absorber is used in the blue matrix film, and more preferably in each of the red, green and blue matrix films, used in dye imbibition printing to attenuate the light in the UV region. A flash exposure is performed on the matrix film with UV light in the substantial absence of light having a wavelength above 410 nm. In accordance with conventional photographic flashing techniques, the flash exposure may be performed either before or after the imagewise exposure. UV absorbing dyes having the required absorption properties which may be used in the matrix films of the invention may be selected from UV absorber dyes described by Besio et al U.S. Patent 4,849,326 (cyano substituted butamines), Logan U.S. Patent 4,839,274 (acetylenic compounds), Pruett et al U.S. Patent 5,215,876 (substituted styrenes), Nishijima et al EPO 0 451 813, Schofield et al EPO 0 190 003, and Umemoto U.S. Patent 5,084,375 (hydroxyphenyl benzotriazoles), Leppard et al EPO 0 531 258 (triazines), Oliver U.S. Patent 3,723,154 (cyanomethyl sulfone-derived merocyanines), Sawdey U.S. Patents 2,739,888, 3,253,921 and 3,250,617 (thiazolidones, benzotriazoles and thiazolothiazoles), Sawdey et al U.S. Patent 2,739,971, Hirose et al U.S. Patent 4,783,394, Takahashi U.S. patent 5,200,307, Tanji et al U.S. Patent 5,112,728, and Leppard et al EPO 0 323 408, Liebe et al EPO 0 363 820, Roth East German DD 288 249, Heller et al U.S. Patent 3,004,896 (triazoles), Wahl et al U.S. Patent 3,125,597 and Weber et al U.S. Patent 4,045,229 (hemioxonols), Diehl et al EPO 0 246 553 (acidic substituted methine oxonols), Leppard et al EPO 0 520 938 and EPO 0 530 135 (triazines), and Liebe et al EPO 0 345 514. Specific examples of UV absorbers are shown below.



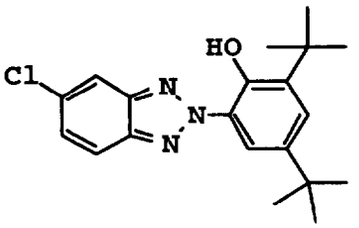
UV-1



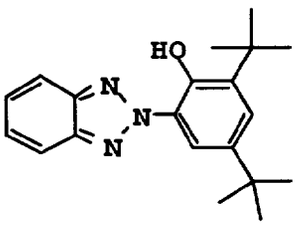
UV-2



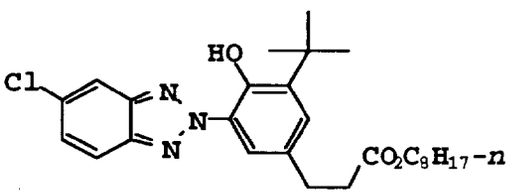
UV-3



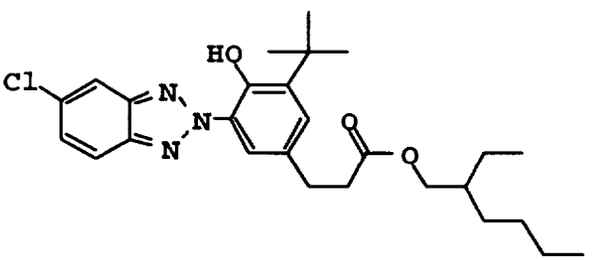
UV-4



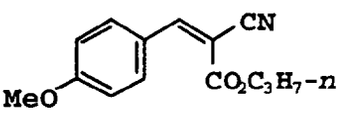
UV-5



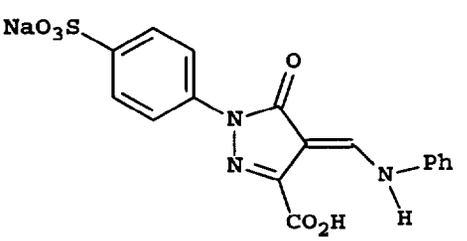
UV-6



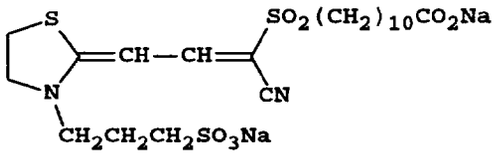
UV-7



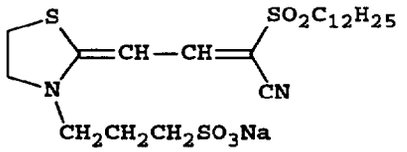
UV-8



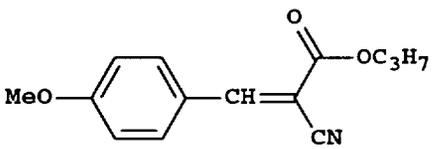
UV-9



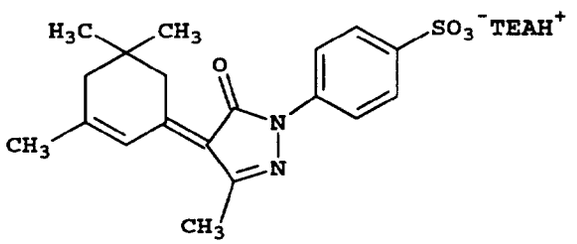
UV-10



UV-11



UV-12



UV-13

The UV absorber is selected according to its spectral characteristics, so as to provide sufficiently high absorption to the UV light flash exposure to decrease the resulting contrast of the matrix film, and sufficiently low absorption above 410 nm such that it does not significantly interfere with the imagewise exposure of the matrix film. A preferred UV absorber absorption spectrum is depicted in Figure 1, which is the absorption spectrum of UV absorber dye UV-1 illustrated above.

In accordance with a preferred embodiment of the invention, the UV flash exposure may be conveniently made, e.g., with a conventional tungsten or tungsten-halogen lamp printer fitted with a filter that transmits UV light and absorbs substantially all visible light above 410 nm. An example of such a filter is a HOYA U-340 filter, the spectral characteristics of which are shown in Figure 2. As such conventional printing lamps do not provide high levels of energy below about 360 nm, the UV absorber preferably has a peak absorbance from 360 to 410 nm, and more preferably from 360 to 390 nm of the absorption spectrum. Of course, the peak absorbance may be at less than 360 nm as long as there is sufficient absorbance between 360 and 410 nm, but this would generally require the use of greater amounts of the UV absorber, which is less preferred. For printing lamps having significant energy below 360 nm, however, the UV absorber may be advantageously selected to provide a corresponding peak absorbance below 360 nm.

In the matrix film light sensitive colloid layer, there are significant levels of light absorbing particles, typically carbon particles, dispersed throughout the layer. In accordance with one embodiment of the invention, a UV dye is also distributed in the colloid layer. The level of contrast control depends on the concentration of the UV dye in the matrix film. As the concentration is increased, the exposure profile of the flash is biased towards the base of the matrix film, where the exposing light is incident. The total silver halide that is available for a sensitometric exposure can be represented as a straight line on a graph of relative exposure vs relative distance from the film base, as in the top line in Figure 3. As the distance from the base is increased, more of the exposure light is absorbed, and therefore the majority of the silver halide at the top of the matrix film layer never receives exposure.

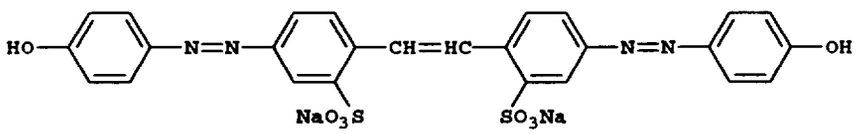
The horizontal axis in Figure 3 is the relative distance from the base of the matrix material, 0.0 is at the base and 1.0 is on the top of the film. The vertical axis is the relative intensity of an exposure through the base. Five levels of UV dye are shown in Figure 3. The levels are such that the optical density of the specific concentration of UV dye in the spectral region used in the exposure correspond to values of 1.0, 2.0, 3.0, 4.0, and 5.0. It is easily seen that as the dye density increases, the bulk of the exposure will reside nearer to the base. In an ideal system, the actual sensitometric contrast which results from filtration will be the original contrast without any filtration reduced by the ratio of the integral of the dyed curves in Figure 3 to the integral of the undyed curve. This technique allows the contrast control of any silver halide grain size in the imbibition matrix film with the proper choice of the UV dye concentration, filter and light source.

The imbibition printing blanks and matrix films described above may contain further features and layers as are known in the art. Preferred supports for such blanks and matrix films comprise transparent polymeric films, such as cellulose nitrate and cellulose esters (such as cellulose triacetate and diacetate), polycarbonate, and polyesters of dibasic aromatic carboxylic acids with divalent alcohols such as poly(ethylene terephthalate).

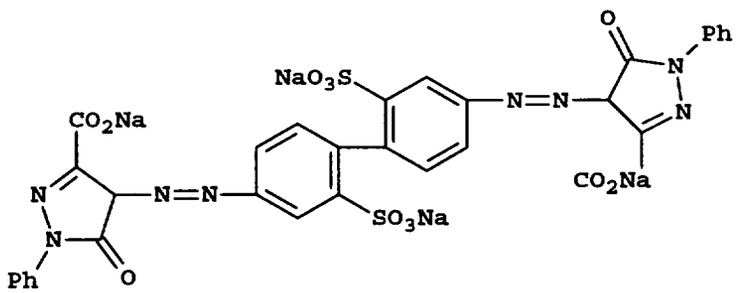
Photographic silver halide emulsion layers may also be included in the printing blanks of the invention. In a motion picture film blank, such a layer may be included between the support and the dye receiving layer as is known in the art in order to enable recording a sound track for the film in accordance with conventional motion picture sound track recording, exposing, and processing procedures. Alternatively, a sound track may be printed on the blank receiver as part of the imbibition printing process.

If desired, the printing blank and matrix films of the invention can be used in conjunction with an applied magnetic layer, such as those described in Research Disclosure, November 1992, Item 34390 published by Kenneth Mason Publications, Ltd., Dudley House, 12 North Street, Emsworth, Hampshire P010 7DQ, ENGLAND.

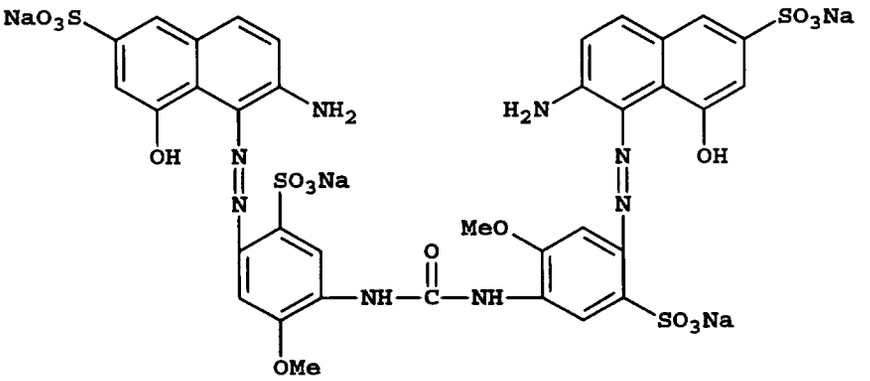
As described above, after imagewise exposure, the colloid layers of such matrix films are typically differentially hardened and removed with a pyrogallol hardening developer as described in U.S. Patent 2,837,430. After formation of colloid relief images in blue, green and red matrix films, the matrix films are dyed with yellow, magenta and cyan dyes, and the dye images are transferred to the mordant-containing receiver film. Exemplary yellow, magenta and cyan dyes which may be used in the imbibition printing process include Y-1, Y-2, M-1, and C-1 illustrated below.



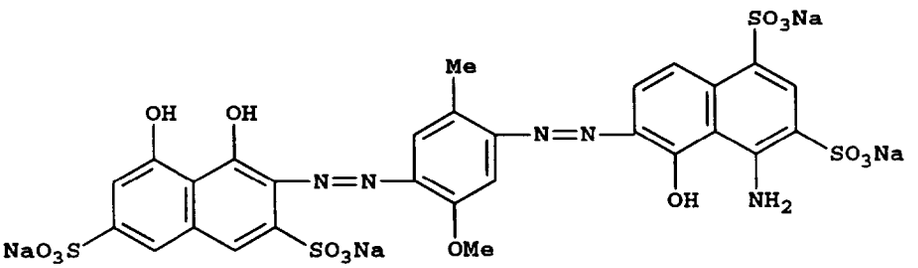
Y-1



Y-2



M-1



C-1

While the plasticizer polymers of one embodiment of the invention have been particularly described in connection with their use in a dye imbibition printing blank receiver, it will be understood that such plasticizers may also be used in other elements which employ a cationic mordant, such as photographic thermal dye transfer receiving layers or antihalation layers, where it is desired to use a plasticizer which does not generate haze in combination with such mordants. The plasticizers of the invention are most advantageous, however, in elements containing printed dye images which are viewed by light projection, such as motion picture films printed by dye imbibition, as it is most desirable to minimize haze in such embodiments.

Plasticizer Polymer Synthesis Example

A latex copolymer having the composition 75 wt % ethylacrylate, 20 wt % styrene, and 5 wt % 2-(N,N,N-trimethylammonium) ethylmethacrylate methosulfate is prepared as follows: to a 500 ml addition flask was added 100 ml of distilled degased water, 1 ml of Igepal CO 730, 1 ml Ethoquad 0/12, 75 g of ethyl acrylate, 20 g of styrene, 6.3 g of 80 % aqueous solution of 2-(N,N,N-trimethylammonium)ethyl methacrylate, and 0.5 g of 2,2'-azobis(2-methylpropionamidine)dihydrochloride. The mixture was stirred under nitrogen. To a 1 L reaction flask was added 300 ml of degased distilled water, 1 ml of Igepal CO 730, 1 ml of Ethoquad 0/12 and 0.5 g of 2,2'-azobis(2-methylpropionamidine)dihydrochloride. The reaction flask was placed in an 80°C bath with stirring and the contents of the addition flask was added over a period of 30 minutes. The contents was stirred at 80°C under nitrogen for 3 hours. The condenser was then removed and the flask was heated to 90°C with a nitrogen purge for 1 hour to remove residual monomer. The flask was then cooled to give a translucent latex containing 24 % solids.

Example 1

Coated dye imbibition printing blank supports were prepared as follows:

Support 1

A 4.7 mil polyethylene terphthalate film support was coated on the backside with a layer containing a copolymer of styrene sulfonic acid sodium salt and 2-hydroxyethyl methacrylate 70/30 wt (182 mg/m^2), a polymer latex of methyl

acrylate, vinylidene chloride, and itaconic acid (15/83/02 wt%) (60 mg/m^2) and Cymel 300 (melamine-formaldehyde resin crosslinking agent from American Cyanamide Co.) (18 mg/m^2) and on the front side with a gel subbing layer containing poly(acrylonitrile-co-vinylidene chloride-co-acrylic acid) (14/80/6 wt%).

Support 2

A 4.7 mil polyethylene terphthalate film support was coated on the backside with a layer containing Nalco 1115 (colloidal silica from Nalco Chemical) (404 mg/m^2), a polymer latex of methylacrylate, vinylidene chloride, and itaconic acid 15/83/02 wt (135 mg/m^2) and on the front side with a gel subbing layer.

Support 3

A 4.7 mil polyethylene terphthalate film support was coated on the backside with a layer containing antimony-doped tin oxide (370 mg/m^2) and Witcobond 232 (polyurethane from Witco Corp.) (125 mg/m^2) and on the front side with a gel subbing layer.

Support 4

A 4.7 mil polyethylene terphthalate film support was coated on the backside with a layer containing antimony-doped tin oxide (226 mg/m^2) and a polymer latex of methyl acrylate, vinylidene chloride, and itaconic acid 15/83/02 wt (75 mg/m^2) followed by a layer containing Witcobond 232 (899 mg/m^2) and on the front side with a gel subbing layer.

Support 5

A 4.7 mil polyethylene terphthalate film support was coated on the backside with a layer containing Witcobond 232 (899 mg/m^2) and on the front side a gel subbing layer followed by a layer containing antimony-doped tin dioxide (296 mg/m^2) and gelatin (52 mg/m^2).

Support 6

A 4.7 mil polyethylene terphthalate film support was coated on the backside with a layer containing Witcobond 232 and a polyaniline imine (1:1 ratio) (108 mg/m^2) followed by a layer containing Elvacite 2041 (polymethylmethacrylate from DuPont) (1076 mg/m^2) and on the front side a gel subbing layer.

Support 7

A 4.7 mil polyethylene terphthalate film support was coated on the backside with a layer containing a polymer of N-vinylbenzyl-N,N,N-trimethylammonium chloride and ethyleneglycol dimethacrylate 93/7 wt (129 mg/m^2) and a polymer of acrylonitrile, vinylidene chloride and N,N-dimethylaminoethyl methacrylate methosulfate 25.1/73.4/1.5 wt (194 mg/m^2) and on the front side a gel subbing layer.

Support 8

A 4.7 mil polyethylene terphthalate film support was coated on the backside with a layer containing a polymer of N-vinylbenzyl-N,N,N-trimethylammonium chloride and ethyleneglycol dimethacrylate 93/7 wt (129 mg/m^2) and a polymer of acrylonitrile, vinylidene chloride and N,N-dimethylaminoethyl methacrylate methosulfate 25.1/73.4/1.5 wt (194 mg/m^2) followed by a layer containing cellulose diacetate (2690 mg/m^2). The front side was coated with a gel subbing layer.

Support 9

A 4.7 mil polyethylene terphthalate film support was coated on the backside with a layer containing vanadium pentoxide (3.2 mg/m^2) and Eastman AQ55D (polyesterionomer from Eastman Chemical Co.) (32 mg/m^2). The front side of the support was coated with a gel subbing layer.

Support 10

A 4.7 mil polyethylene terphthalate film support was coated on the backside with a layer containing vanadium

pentoxide (296 mg/m^2) and Eastman AQ29D (polyesterionomer from Eastman Chemical Co.) (3.2 mg/m^2) followed by a layer containing Witcobond 232 (899 mg/m^2) and the front side was coated with a layer containing a gel sub well known in the art.

Support 11

A 4.7 mil polyethylene terphthalate film support was coated on the backside with a layer containing Elvanol 71-30 (polyvinylalcohol from DuPont) (54 mg/m^2), Volan (methacrylato chromic chloride from DuPont) (1.9 mg/m^2) and potassium nitrate (5.4 mg/m^2). The front side of the support was coated with a gel subbing layer.

Support 12

A 5 mil polyethylene terphthalate film support was coated on the backside with a layer containing vanadium pentoxide (3.2 mg/m^2) and a polymer latex of acrylonitrile, vinylidene chloride and acrylic acid 15/9/76 wt (2.4 mg/m^2) followed by a layer containing Elvacite 2041 (1064 mg/m^2). The front side of the support was coated with a gel subbing layer.

Control Support

A 4.7 mil polyethylene terphthalate film support was coated on the backside with a layer containing Witcobond 232 (899 mg/m^2) and on the front side with a gel subbing layer.

Dye imbibition printing blank Samples 1-12 and a Control Sample were made using corresponding Supports 1-12 and the Control Support as follows. Each support was coated on the front side with a layer containing silver bromoiodide emulsion (1940 mg/m^2 Ag), EDTA sodium salt (83.2 mg/m^2), methylbensothiazolium chloride (10.1 mg/m^2), gelatin (3500 mg/m^2) and bisvinylsulfonylmethyl ether (75.6 mg/m^2) followed by a layer containing polymer of copoly (N-vinylbenzyl-N,N,N-trimethylammonium chloride-co-ethyleneglycol dimethacrylate) 93/7 mole (861 mg/m^2), Olin 10G surfactant (97.3 mg/m^2), potassium nitrate (39.7 mg/m^2), gelatin (2800 mg/m^2), and a polymer methacrylate methosulfate 75/25/5 wt (280 mg/m^2).

The surface electrical resistivity and the water electrode resistivity for certain of the above coatings were measured. The results are indicated in Table I below.

Table I

Sample	Surface Electrical resistivity (ohm/square, 20% RH)	Water Electrode resistivity (ohm/square, 20% RH)
1	2×10^{10}	
2	6×10^{11}	
3	5×10^{8}	
5		1×10^{9}
6		1×10^{9}
7	5×10^{9}	
8		4×10^{9}
9	1×10^{9}	
10		1×10^{8}
11	$>3 \times 10^{14}$	
12		1×10^{7}
Control	$>3 \times 10^{14}$	4×10^{11}

Desired resistivity values for surface electrical resistivity are less than about 10^9 and for water electrode resistivity are less than about 10^9, and especially less than about 10^8 ohm/square. While all antistatic materials will improve resistivity levels to some extent, the metal oxide containing antistatic layers of Samples 3, 5, 9, 10, and 12 demonstrate especially preferable results. It is also noted the antistat in Sample 1 is not photographic development process surviving, and therefore not preferred.

An unwinding electrification test is used to determine if there is a "discharge" or "glow" in the unwinding nip of a roll of light sensitive film during production or handling. During this test a roll of film is unwound at a high speed. If there is a large separation charge, due to the fact that two dissimilar materials are being separated, the electric field in the unwind nip will be large. It can be large enough such that the air can no longer sustain the intense field and air breakdown

will occur resulting in a static discharge. Such discharge can potentially be harmful to a light sensitive emulsion which may be used for recording a sound track in an imbibition printing blank. Table II shows the results of such an unwinding electrification test which was performed on Samples 7, 8, 11 and 12.

Table II

Sample	Glow observed
11	yes
7	yes
8	yes
12	no

Retransfer of dye from the printed front side of a dye imbibition print to the backside during storage in the roll can be a problem especially at high humidity and temperature. An antistatic backing layer can play an important part in this retransfer. To check for dye retransfer, the front sides of imbibition prints dyed with magenta dye M-1 were placed in contact with the backsides of each of Samples 1-12 and the Control Sample between two glass plates, and the assemblage was then placed in a chamber at 80 percent relative humidity and 38°C for four days. The backs of the undyed imbibition prints were then observed for the presence of transfered dye. The results are shown in Table III.

Table III

Sample number	Dye present
1	no
2	no
3	no
4	no
5	no
6	no
7	yes
8	no
9	no
10	no
11	no
12	no
control	no

Antistatic backings that contain a cationic polymeric material as in Sample 7 can result in dye retransfer as indicated above. Overcoating this antistat layer with a polymer as in Sample 8 may solve this retransfer problem, but poorer antistatic properties result.

In accordance with the most preferred embodiments of the invention, Samples 3, 5, 9, 10, and 12 meet the desired attributes of desired resistivity, no glow discharge and no dye retransfer. These examples all contain metal oxide antistats.

Example 2

Dye imbibition printing blanks were prepared as follows:

Component	Coverage
Top layer:	
Mordant: copoly(N-vinylbenzyl-N,N,N-trimethylammoniumchloride co-ethyleneglycol dimethacrylate) 93/7 mole ratio	861 mg/m^2
Olin 10G surfactant	97.3 mg/m^2
KNO_3 antistatic agent	39.7 mg/m^2
gelatin	2799 mg/m^2

(continued)

Component	Coverage
Top layer:	
plasticizer polymer PP-1	280 mg/m^2
Bottom layer:	
EDTA sodium salt	83.2 mg/m^2
Methylbenzothiazolium chloride	10.1 mg/m^2
Gelatin	3498 mg/m^2
Bisvinysulfonylmethyl ether	75.6 mg/m^2

Support:

A 4.7 mil polyethylene terphthalate film support coated on the backside with a layer containing Elvanol 71-30 (polyvinylalcohol from DuPont) (54 mg/m^2), Volan (methacrylato chromic chloride from DuPont) (1.9 mg/m^2) and potassium nitrate (5.4 mg/m^2).

Additional blanks were prepared substituting plasticizer polymers PP-2, PP-3 and PP-4 and comparative plasticizer polymers C-1, C-2 and C-3 for PP-1 at equal weights.

C-1 poly(methyl acrylate)
C-2 poly(ethyl acrylate)
C-3 poly(ethyl acrylate-co-styrene) 80/20 wt

The haze of each coating was measured after drying using a XL-211 Hazegard system manufactured by BYK-gardner which measures the transmitted light passed through a sample. The results are presented in Table IV below:

Table IV

Plasticizer Polymer	%Haze
None	1.5
PP-1	1.4
PP-2	1.4
PP-3	1.4
PP-4	1.2
C-1	7.5
C-2	2.9
C-3	4.1

As demonstrated above, plasticizer polymers other than those in accordance with the preferred embodiments of the invention in the presence of the mordant in the coating composition can cause hazy coatings to occur upon drying. This difficulty is overcome by using the plasticizer latex of the preferred embodiments of the invention.

Example 3

The effectiveness of plasticizer latex in accordance with the preferred embodiments of the invention at reducing brittleness was also demonstrated. A dye imbibition printing blank was made as described in Example 2, with PP-5 in place of PP-1 at the indicated coverages. The brittleness test performed provides for quantitatively measuring the brittleness of film by subjecting it to bending. By means of a wedge, the diameter of a film loop was constantly changed through gradually decreasing openings until a failure of the film resulted. The opening of the wedge at which the film failed is the measure of its brittleness. The film was conditioned at 15 percent relative humidity and 21°C before running the test. The smaller wedge opening before the onset of failure the more flexible the film.

Table V

Example	Polymer level mg/m^2	Brittleness (relative wedge opening at failure)
2.1 (comparison)	0	0.20
2.2 (invention)	215	0.11
2.3 (invention)	430	0.08

Table V shows the effectiveness of the plasticizer latex of the invention to give acceptable coatings with reduced brittleness.

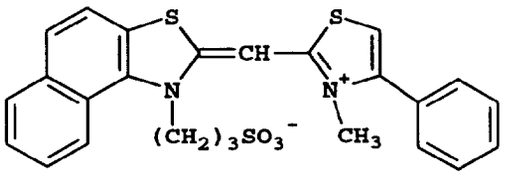
Example 4

Blue light sensitive matrix films were coated with different levels of the UV absorber dye UV-1 (0.0, 135, 269, and 538 mg/m^2). The format below was used for the experiments of this example:

Component	Coverage
Top Layer	
Gelatin	883 mg/m^2
Carbon	323 mg/m^2
Semicarbazide.HCl	34 mg/m^2
Triton X-200E (commercial surfactant)	12 mg/m^2
Silver Halide Layer	
Gelatin	9688 mg/m^2
Carbon	538 mg/m^2
Sensitized emulsion (cubic Ir-doped AgBrI with 3.4 mole% iodide and 0.21 cubic edge length, spectrally sensitized with blue sensitizing dye BSD-1)	2422 mg/m^2
Potassium nitrate	255 mg/m^2
UV absorber dye UV-1, when used	various mg/m^2

Support

5 mil clear polyester film support coated on the backside with a layer containing vanadium pentoxide (3.2 mg/m^2) and a polymer latex of acrylonitrile, vinylidene chloride and acrylic acid 15/9/76 wt (2.4 mg/m^2) followed by a layer containing Elvacite 2041 (1064 mg/m^2). The front side of the support was coated with a gel subbing layer.



BSD-1

The Top Layer described above was provided to improve uniformity of the coating, processing, and antistatic performance of the matrix films, but is not necessarily required for the matrix films in accordance with the invention.

The matrix films were exposed through a 21 step tablet on a sensitometer with a conventional tungsten lamp printer fitted with a HOYA U-340 filter (the spectral characteristics of which are shown in Figure 2) and processed with a pyrogallol hardening developer as described in U.S. Pat. no. 2,837,430 to form a relief record. The resulting sensitometric curves for the matrix films are shown in Figure 4. As is evident from Figure 4, the contrast of the matrix films decreased as the UV dye concentration increased. The Best Fit Contrast (the slope of the best straight line which fits the contrast of the sensitometric curve) of the four levels of UV dye are plotted in Figure 5. Within this range, any contrast can be attained for a flash exposure with the proper dye concentration, which in combination with an imagewise exposure enables effective and selective toe contrast control for the resulting relief image.

Example 5

Not all UV absorbers will work effectively with conventional tungsten or tungsten-halogen lamp printers fitted with a filter that transmits UV light and absorbs substantially all visible light above 410 nm. The peak wavelength of the UV absorber selected for use with such printers is preferably above 360 nm (but still below 410 nm), as tungsten lamps typically have minimal energy below 360 nm. The native blue sensitivity of the silver halide is active within this 360-410 nm wavelength range. If the UV dye absorption peak is relatively short (such as 350 nm), it may not have the ability to attenuate light in the range where a tungsten or tungsten-halogen lamp produces energy and the matrix film senses the energy.

Example 4 was essentially repeated, except for substituting a mixture of UV absorber dyes UV-2 and W-3 for dye UV-1. A comparison of the UV absorbers is shown in Figure 6, where the absorbance spectrum on the right in Figure 6 with the longer wavelength peak is that of dye UV-1, while absorbance spectrum on the left in Figure 6 with the shorter wavelength peak is that of the mixture of dyes UV-2 and UV-3. Figure 7 shows the sensitometry of the experimental results. The three curves plotted are three similar blue matrix films with 0.0 mg UV dye, 269 mg/m^2 of UV-1 and 269 mg/m^2 of UV-2/UV-3. The sensitometry of the matrix film without dye and the matrix film with 269 mg/m^2 of the shorter peaked absorber dyes (UV-2/UV-3) are similar in contrast. Thus, the shorter peaked UV absorber did not work in this case in combination with a tungsten lamp UV flash to reduce contrast, while the matrix film with 269 mg/m^2 of UV-1 did exhibit a large contrast change.

Example 6

Red and green light sensitive matrix films of the following formats were coated with different levels of the UV absorber dye UV-1 and exposed and processed similarly as described in Example 4.

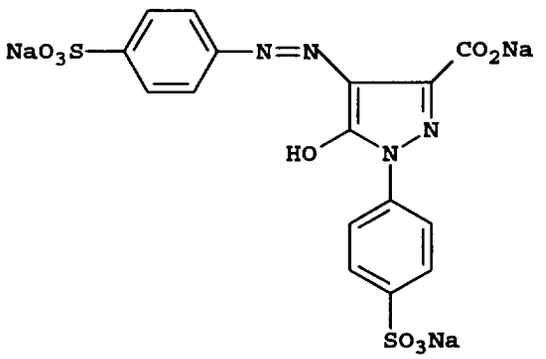
Component	Coverage	
	(Red Matrix)	(Green Matrix)
Silver Halide Layer		
Gelatin	10764 mg/m^2	9688 mg/m^2
Carbon	431 mg/m^2	538 mg/m^2
Sensitized emulsion	1938 mg/m^2 (cubic Ir-doped AgBrI with 3.4 mole% iodide and 0.13 cubic edge length, spectrally sensitized with red sensitizing dye RSD-1)	1722 mg/m^2 (cubic Ir-doped AgBrI with 3.4 mole% iodide and 0.09 cubic edge length, spectrally sensitized with green sensitizing dyes GSD-I and GSD-2)

(continued)

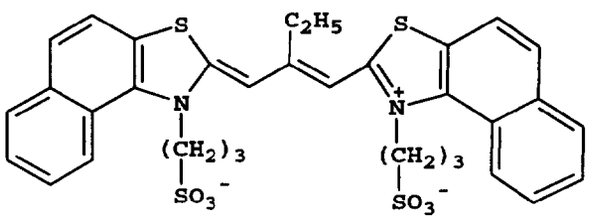
Component	Coverage	
	(Red Matrix)	(Green Matrix)
Silver Halide Layer		
Yellow dye YD-1	2368 mg/m^2	2799 mg/m^2
UV absorber dye UV-1	various mg/m^2	various mg/m^2

Support

5 mil clear polyester film support coated on the backside with a layer containing vanadium pentoxide (3.2 mg/m^2) and a polymer latex of acrylonitrile, vinylidene chloride and acrylic acid 15/9/76 wt (2.4 mg/m^2) followed by a layer containing Elvacite 2041 (1064 mg/m^2). The front side of the support was coated with a gel subbing layer.

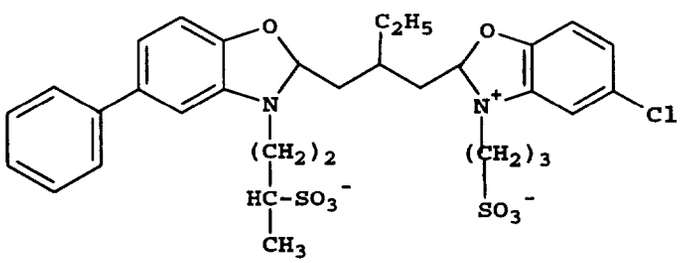


YD-1



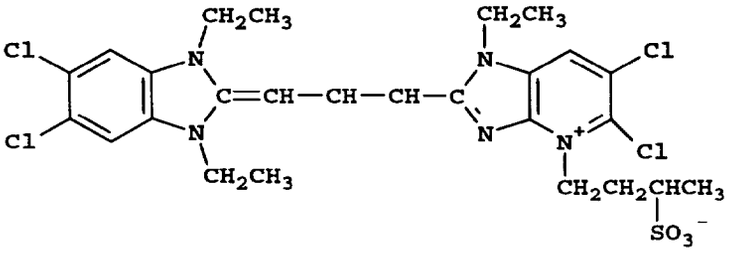
RSD-1

$HN^+(C_2H_5)_3$



GSD-1

Na^+



GSD-2

The matrix films contained further conventional photographic coating addenda well known in the art. Similar contrast reduction for the red and green matrix films was observed dependent upon the UV absorber concentration as was observed for the blue matrix films of Example 1.

Claims

1. A dye imbibition printing blank comprising a support bearing on one side thereof a dye-receiving layer comprising a cationic mordant, wherein the printing blank further comprises an antistatic layer substantially free of cationic polymers.

2. A printing blank according to claim 1, wherein the antistatic layer is provided on the opposite side of the support relative to the dye-receiving layer.

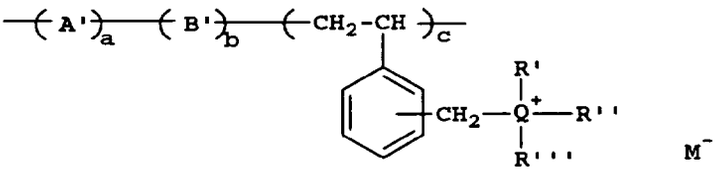
3. A printing blank according to claim 1 or claim 2 wherein the antistatic layer comprises an anionic polymer, electronic conducting non-ionic polymer, metal halide or metal oxide.

4. A printing blank according to any one of claims 1-3 wherein the antistatic layer comprises a metal oxide and a polymer binder.

5. A printing blank according to claim 4, further comprising a protective polymeric overcoat layer on the antistatic layer.

6. A printing blank according to any one of claims 1-5, wherein the cationic mordant is a quaternary ammonium or phosphonium mordant.

7. A printing blank according to claim 6, wherein the cationic mordant is of the formula:



wherein A' represents units of an addition polymerizable monomer containing at least two ethylenically unsaturated groups; B' represents units of a copolymerizable α,β-ethylenically unsaturated monomer; Q is N or P; R', R", and R"' are independently carbocyclic or alkyl groups; M^- is an anion; a is from 0.25 to 10 mole percent; b is from 0 to 60 mole percent; and c is from 40 to 99 mole percent.

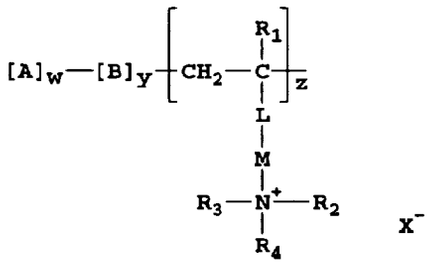
8. A printing blank according to any one of claims 1-7, wherein the dye receiving layer further comprises a hydrophillic colloid and a plasticizer polymer, wherein the plasticizer polymer is a latex polymer having a glass transition temperature below 30°C comprising from 2 to 20 weight percent of units having a quaternary ammonium group.

9. A dye imbibition printing blank comprising a support bearing a dye-receiving layer comprising a cationic mordant, a hydrophillic colloid, and a plasticizer polymer, wherein the plasticizer polymer is a latex polymer having a glass

transition temperature below 30°C comprising from 2 to 20 wt% of units having a quaternary ammonium group.

10. A printing blank according to claim 8 or claim 9, wherein the plasticizer polymer is a vinyl co-polymer and wherein the units having a quaternary ammonium group are acrylic or methacrylic esters or amides to which the quaternary ammonium group is appended.

11. A printing blank according to claim 10, wherein the plasticizer polymer is of the formula



wherein A represents units derived from an acrylic or methacrylic ester monomer; B represents units derived from a vinyl benzene monomer; R_1 is H or methyl; L is -C(O)O-, -C(O)NH-, or an aromatic linking group; M is a C_1 to C_{12} alkenyl linking group; R_2, R_3, and R_4 are C_1 to C_6 alkyl groups; X^- is an anionic counterion; w is 50 to 98 weight percent; y is 0 to 48 weight percent; and z is 2 to 20 weight percent.

12. A printing blank according to any one of claims 1-11, wherein the support is transparent.

13. A printing blank according to any one of claims 1-12, further comprising a silver halide emulsion layer for recording a sound track.

14. A process for exposing a dye imbibition printing matrix film comprising imagewise exposing a matrix film comprising a visible light sensitive silver halide emulsion containing colloid layer on a support to blue, green or red light, wherein the visible light sensitive emulsion is also sensitive to UV light and the toe contrast of the imaged matrix film is controlled by (i) incorporating a UV absorber in the colloid layer of the matrix film, and (ii) flash exposing the matrix film with UV light in the substantial absence of light having a wavelength above 410 nm, wherein the UV absorber provides sufficiently low absorption above 410 nm such that it does not substantially alter the effective photographic speed of the matrix film during the imagewise exposure or the mid scale contrast of the imaged matrix film, and sufficiently high absorption to the UV light to decrease the resulting toe contrast of the imaged matrix film.

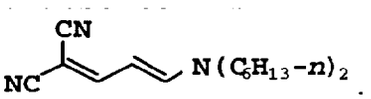
15. A process according to claim 14, wherein the matrix film comprises a blue light sensitive silver halide emulsion which is imagewise exposed to blue light.

16. A process according to claim 14, wherein the matrix film comprises a pan-sensitive silver halide emulsion.

17. A process according to any one of claims 14-16, wherein the flash UV exposure is performed with a tungsten or tungsten-halogen lamp and a filter that transmits UV light and absorbs substantially all light above 410 nm.

18. A process according to any one of claims 14-17, wherein the UV absorber has peak absorbance between 360 and 390 nm.

19. A process according to any one of claims 14-17, wherein the UV absorber is



20. A matrix film for use in imbibition printing comprising a support bearing a colloid layer comprising (i) a visible light sensitive silver halide emulsion which is also sensitive to UV light, (ii) visible light absorbing non-photosensitive

particles, (iii) a hydrophilic colloid, and (iv) a UV absorber having a peak absorbance between 360 and 410 nm.

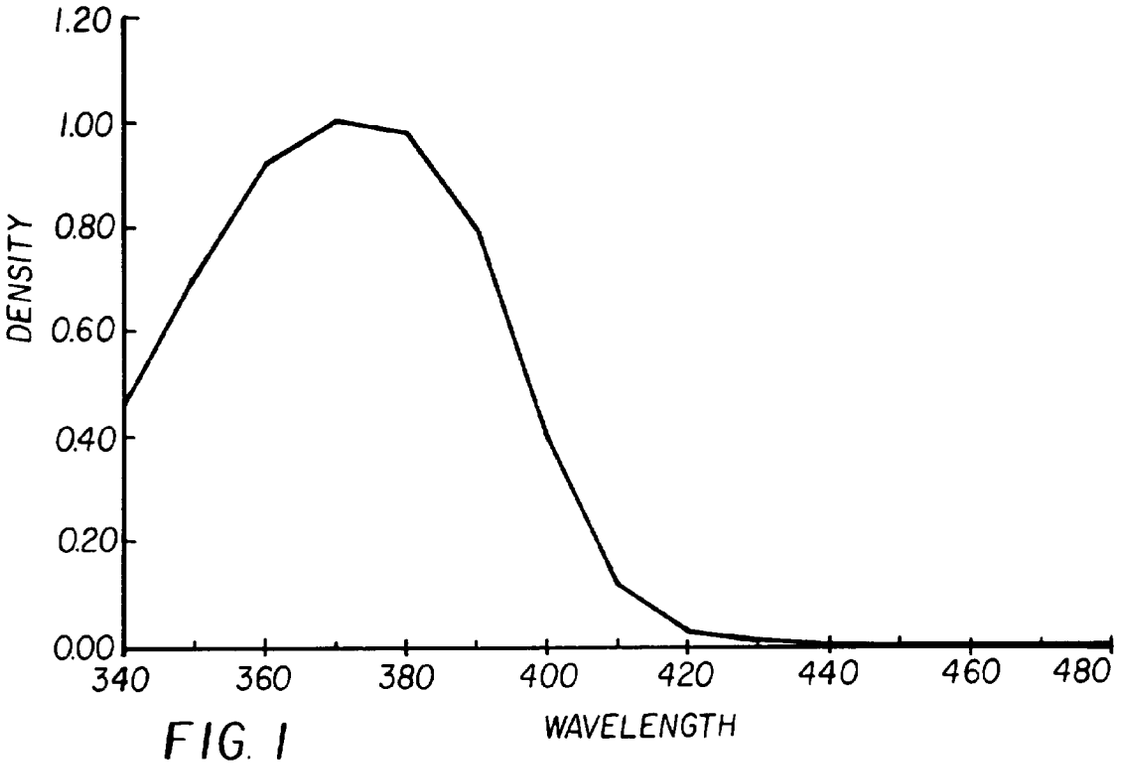

1.20
1.00
0.80
0.60
0.40
0.20
0.00
DENSITY
340
360
380
400
420
440
460
480
WAVELENGTH

FIG. 1

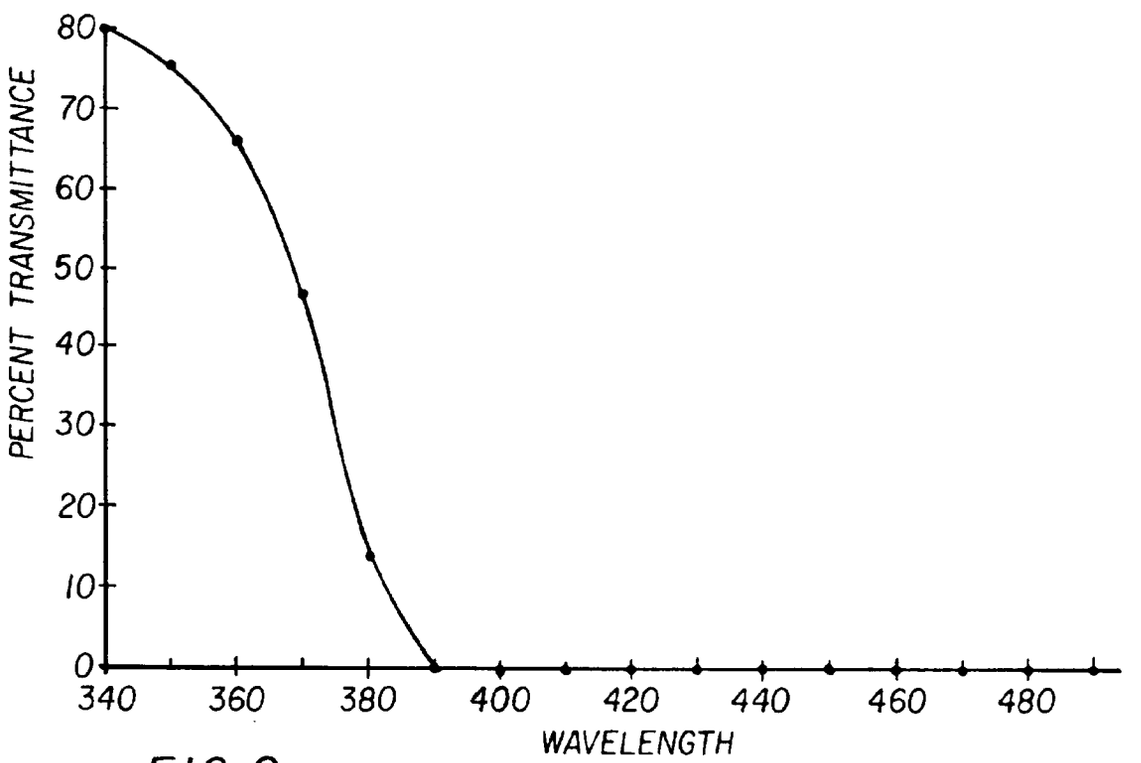

80
70
60
50
40
30
20
10
0
PERCENT TRANSMITTANCE
340
360
380
400
420
440
460
480
WAVELENGTH

FIG. 2

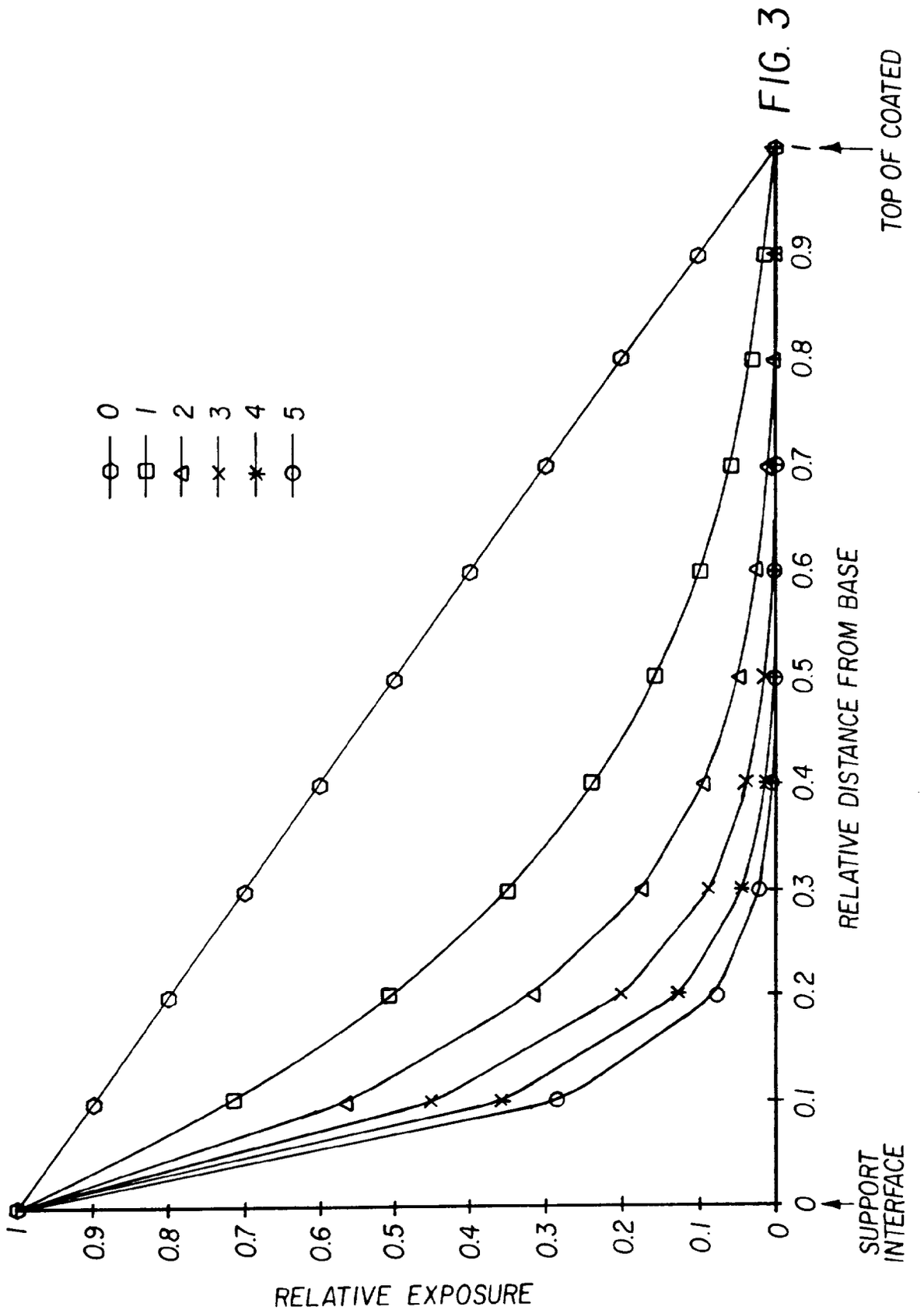

0
1
2
3
4
5
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
RELATIVE EXPOSURE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
SUPPORT INTERFACE
RELATIVE DISTANCE FROM BASE
TOP OF COATED

FIG. 3

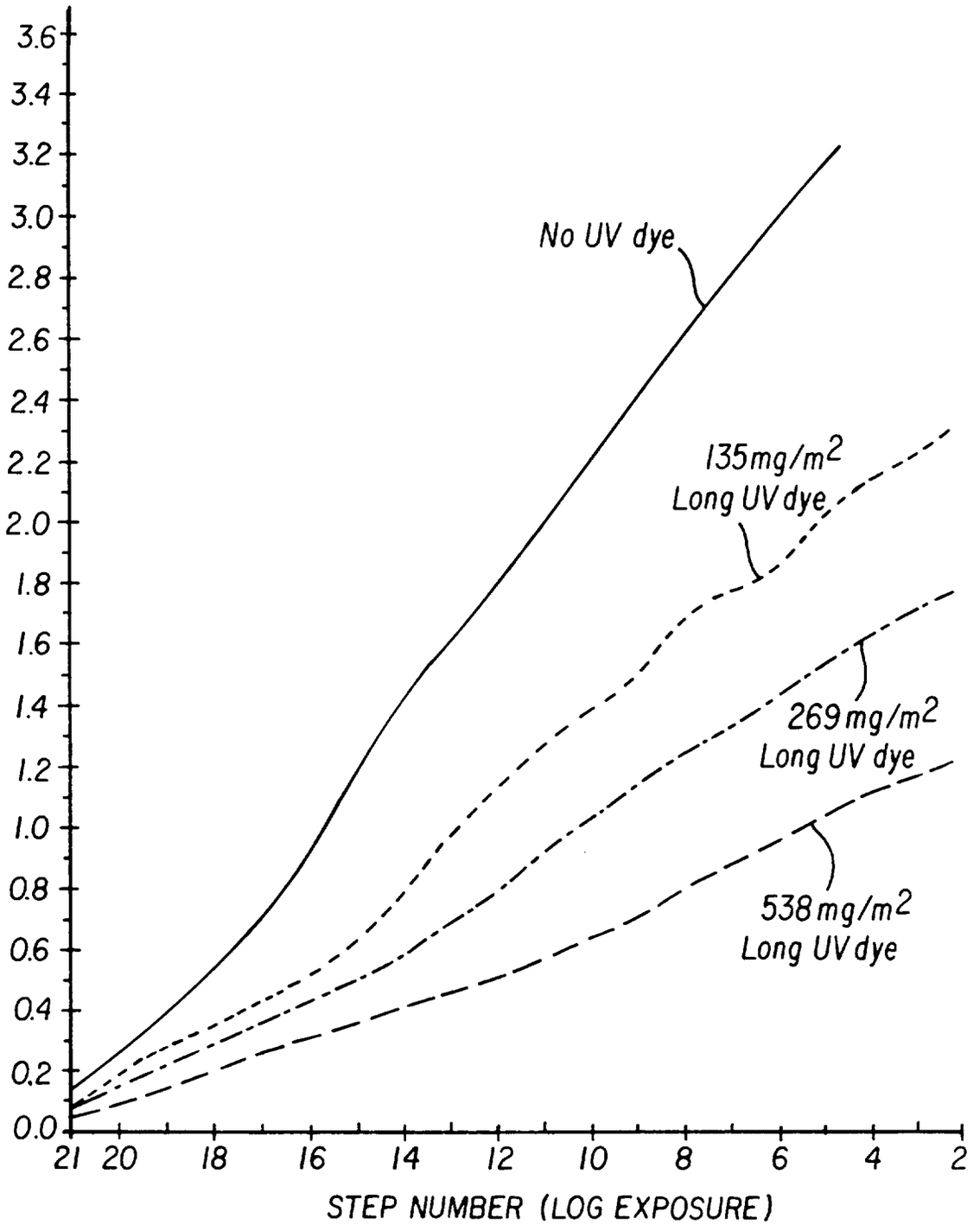

3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
No UV dye
135mg/m2
Long UV dye
269mg/m2
Long UV dye
538mg/m2
Long UV dye
21 20 18 16 14 12 10 8 6 4 2
STEP NUMBER (LOG EXPOSURE)

FIG. 4

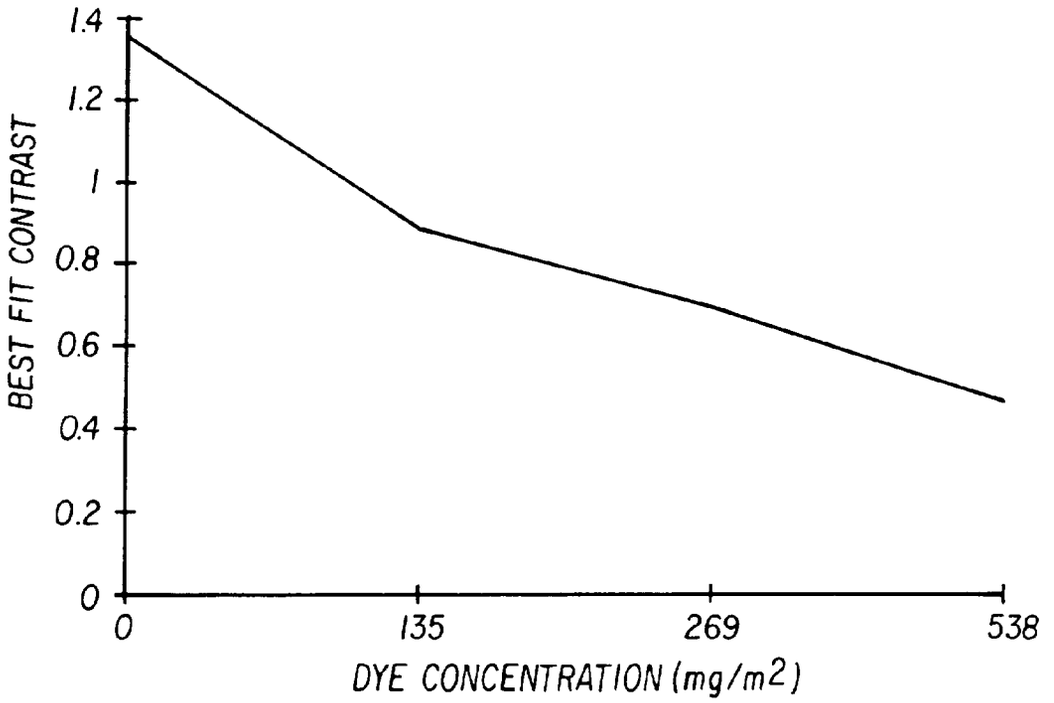

1.4
1.2
1
0.8
0.6
0.4
0.2
0
BEST FIT CONTRAST
0
135
269
538
DYE CONCENTRATION (mg/m2)

FIG. 5

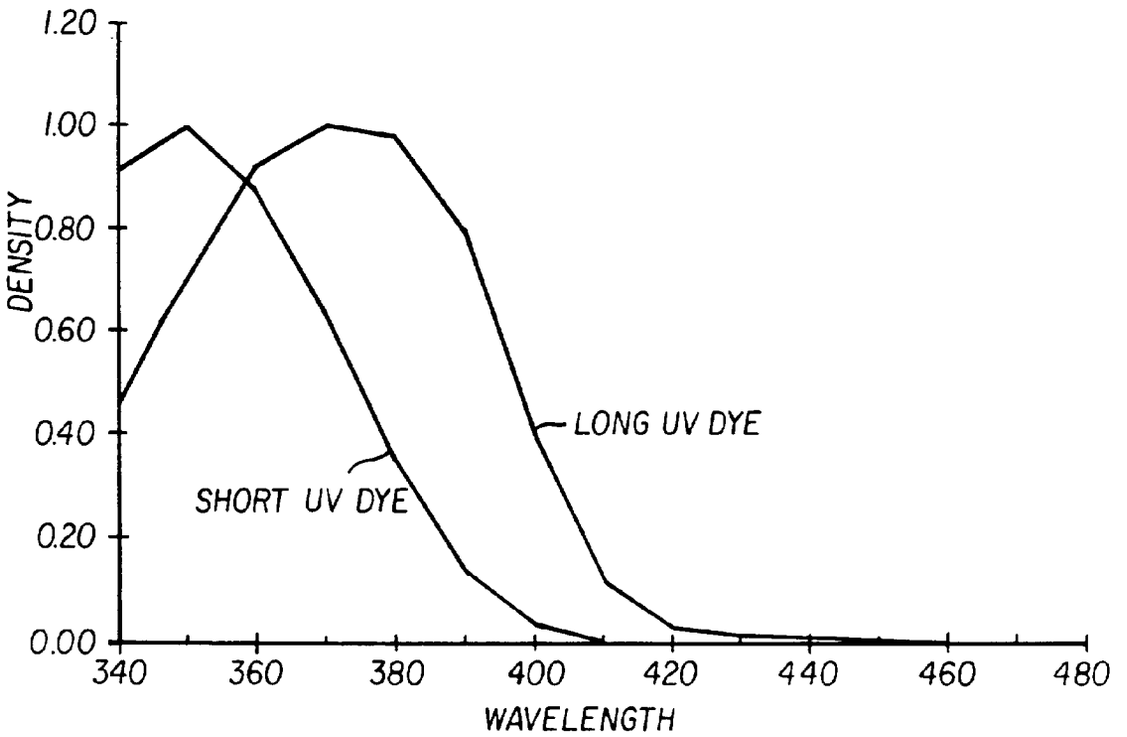

1.20
1.00
0.80
0.60
0.40
0.20
0.00
DENSITY
LONG UV DYE
SHORT UV DYE
340
360
380
400
420
440
460
480
WAVELENGTH

FIG. 6

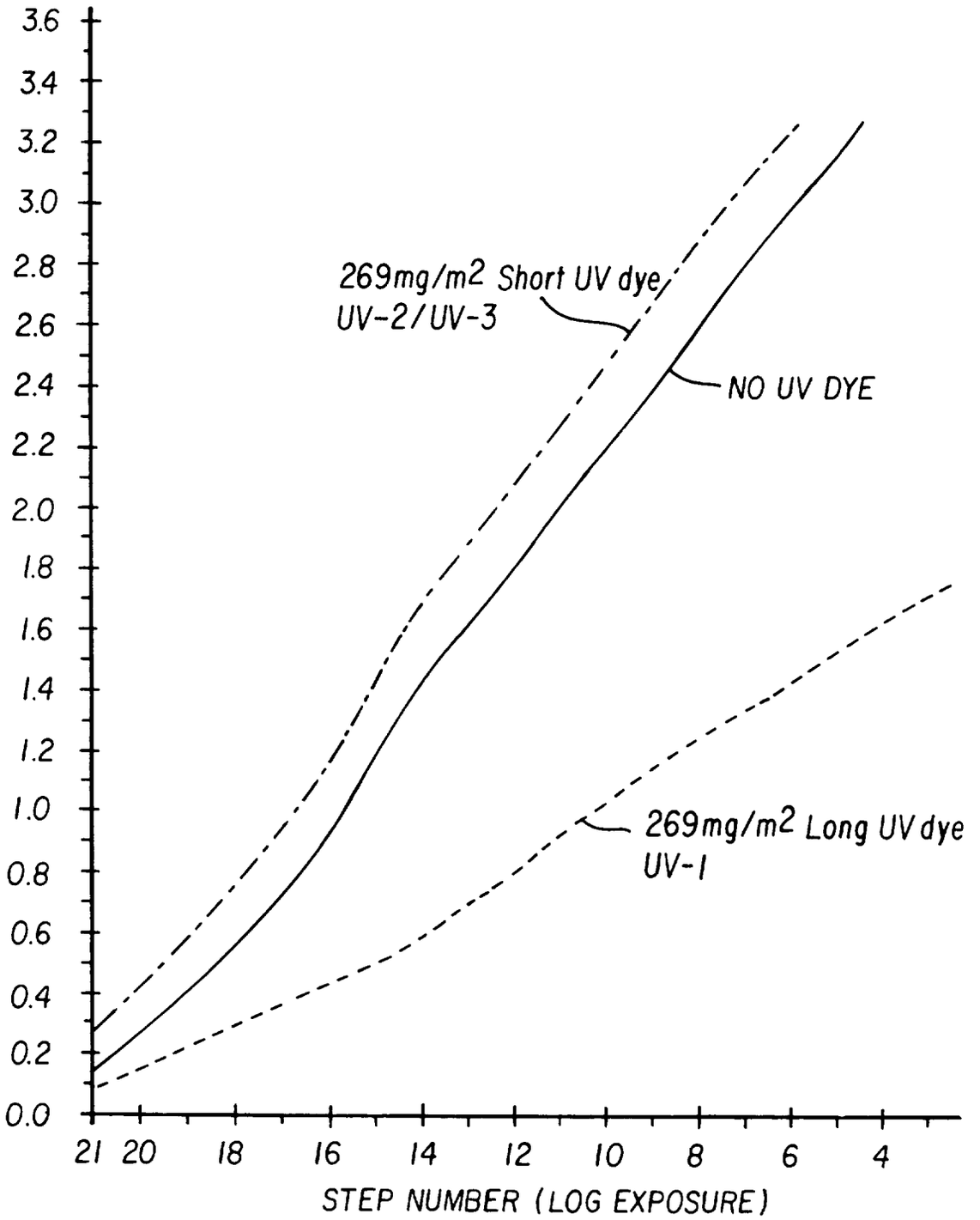

3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
269mg/m2 Short UV dye
UV-2/UV-3
NO UV DYE
269mg/m2 Long UV dye
UV-1
21 20 18 16 14 12 10 8 6 4
STEP NUMBER (LOG EXPOSURE)

FIG. 7