

[54] **OPAQUE PHOTOGRAPHIC FILM SUPPORT**

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96/87 A, 117/76

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[58] Field of Search **96/85, 87 R, 84 M, 84 R**

[56] **References Cited**

UNITED STATES PATENTS

3,320,191	5/1967	Secrist.....	96/87 R
3,635,713	1/1972	Van Paesschen et al.....	96/85
3,295,979	1/1967	Secrist et al.	96/87 R

FOREIGN PATENTS OR APPLICATIONS

993,781 6/1965 Great Britain 96/85

Primary Examiner—Ronald H. Smith

[57] **ABSTRACT**

An opaque element comprises a flexible transparent film support, such as a polyester support, having thereon a first layer containing carbon black, casein and a compatible organic polymeric material over which is coated a contiguous second layer comprising casein and a compatible organic polymeric material such as a polyvinyl acetate or a styrene-acrylic acid polymer which improves the cracking resistance. The element may be a support for a light-sensitive layer or for an image receiving layer of the type used in an image transfer system.

15 Claims, No Drawings

OPAQUE PHOTOGRAPHIC FILM SUPPORT**FIELD OF THE INVENTION**

This invention relates to opaque layers particularly opaque layers for coating on a transparent film support such as a polyester support. A first layer comprises a pigmented opaque layer over which is coated a contiguous non-pigmented second layer which improves the cracking resistance of the first layer.

For many reasons it is desirable to have photographic elements which have an opaque layer on the film support. For instance, in image transfer systems, it is advantageous to remove the exposed film from the camera to a light environment before processing is complete. Under such conditions, it is necessary to prevent further exposure of the photosensitive layer before processing is complete. Various methods which permit white light processing are known such as that disclosed in Canadian Patent 682,226 issued Mar. 17, 1964 to Campbell et al. In order to provide the opacity to the supports used for the light sensitive element and for the image receiving element, each support comprises two or more strata possessing different optical properties such as, for example, a light-absorptive stratum and a diffusely or specularly reflective stratum or the like.

Optical flaws such as minute pinholes, breaks, etc., permit the leakage or penetration of light therethrough in many opaque coatings. The necessity for at least two opaque strata, for example, a metallic, radiation-reflective strata such as aluminum in combination with a diffusely reflective strata such as white or black paper or a sort of a medium containing a dispersed white pigment, e.g., titanium dioxide or the like, results in a thick element which has disadvantages particularly in image or diffusion transfer processes where the sensitized photographic element after exposure is drawn around an arcuate guide member into contact with a receiving sheet. The arcuate guide member is usually of such configuration that the photographic element must be bent at a sharp radius to pass thereover. Therefore, it has been desirable to provide a flexible element which is opaque and is relatively free from pinholes and cracking.

Accordingly, one object of this invention is to provide a photographic element having only one opaque layer. A further object is to provide a flexible support such as a polyester having thereon an opaque coating. An additional object is to provide a two-coat layer system for flexible polymeric supports in which one layer contains an opaquing pigment. Another object is to provide a second coat over a first opaque coating which reduces pinholes and cracking of the opaque coating. Still another object of this invention is to provide a photographic silver halide element or a diffusion transfer receiving sheet comprising a support having such coatings thereon.

SUMMARY OF THE INVENTION

According to this invention, there is provided an element comprising a flexible support such as a polyester having thereon a first opaque layer comprising casein, an opaquing pigment such as carbon black, and a compatible organic polymeric film-forming material and a second layer contiguous thereto comprising casein and a compatible organic polymeric film-forming material.

In a preferred embodiment, a polyester support such as polyethylene terephthalate is coated with (1) a first layer comprising a hydrophilic opaque coating comprising casein, carbon black and a compatible organic polymeric material such as polyvinyl acetate or a styrene-acrylic acid polymer, and (2) a second layer comprising casein and a compatible polymeric material such as polyvinyl acetate or a styrene-acrylic acid polymer.

DESCRIPTION OF PREFERRED EMBODIMENTS

Flexible supports which are particularly useful are prepared from polyesters, particularly from polyesters of glycols and terephthalic acid. A particularly useful polyester is polyethylene terephthalate. Other suitable polyesters can be prepared by the esterification with a suitable glycol of a dicarboxylic acid, e.g., terephthalic acid, or by alcoholysis of esters or other terephthalic acid compounds capable of reacting with glycols to form glycol esters as disclosed in Whinfield et al U.S. Pat. No. 2,465,319 of Mar. 22, 1949. Photographic films having a polyester base, e.g., a highly polymeric linear polyester of a dicarboxylic acid with a dihydric alcohol are described in Carothers U.S. Pat. No. 2,216,736. Swindells U.S. Pat. No. 2,698,235 of Dec. 28, 1954 discloses that a good anchorage can be obtained between a polyester photographic film base and gelatin layers if a very thin layer of a tri-component polymer of vinylidene chloride an acrylic ester and itaconic acid is coated on the polyester photographic film under controlled conditions. Alles et al U.S. Pat. No. 2,627,088 of Feb. 3, 1953 teaches that the improved anchorage, obtained when polyester films are coated with the resin made from vinylidene chloride/acrylic ester/itaconic acid copolymer, is not affected by actually stretching the coated film at an elevated temperature.

Other flexible sheeting material may, of course, be used as flexible supports according to the practice of this invention and include e.g., paper, paper having a polymeric overcoat such as polyethylene or other polymer, polycarbonates, polyacetals, polystyrene, cellulose organic esters, such as cellulose triacetate, cellulose nitrate, cellulose acetate butyrate, cellulose acetate, polyolefins such as polyethylene and the like.

The polymeric surface of the support can be treated to improve the adhesion of subsequent layers e.g., radiation-sensitive layers or the like using suitable techniques known to the art. Typical treatments which are particularly suitable for use with hydrophobic polymers such as polyesters, polyolefins, etc. include treatments with a flame, use of an oxidizing agent such as nitric acid, sodium hypochlorite, chlorine, hydrogen peroxide, sulfuric acid and potassium chromate, etc., corona discharge, radiation by ultraviolet light, etc.

Another method of improving the adhesion of layers to a polymer coated surface is illustrated by Alsup U.S. Pat. No. 3,161,519 issued Dec. 15, 1964, in which colloidal silica is employed in a coating over a polyolefin surface. In the particular disclosure therein, a coating mixture containing colloidal silica is coated on untreated polyethylene coated paper and dried with hot air at about 150°F.

The first opaque layer on the support comprises casein, an opaque pigment and a compatible polymeric material. A particularly useful opaque pigment is carbon black which may be prepared by any of the usual

methods but any opaquing pigment may be used. Preferably black pigments are used but any pigment can be used including barium sulfate, zinc oxide, titanium oxide, barium stearate, silver flakes, silicates, alumina, zirconium oxide, zirconium acetyl acetate, sodium zirconium sulfate, kaolin, mica, titanium dioxide, zinc sulfide, cadmium sulfide, magnesium oxide, nickel oxide, nickel sulfide, lead iodide, etc.

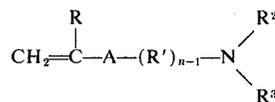
Suitable pigments can for instance be selected from the various classes of readily dispersible pastes and pigments which usually contain a wetting agent as an adjuvant. More specific examples of suitable pigments are Microsol Schwartz 2B paste (trade name for an aqueous carbon black dispersion), etc.

The second contiguous layer comprises casein and a polymeric material. This may be the same or different polymeric material as that used in the opaque layer. The second layer may also contain the same coating aids, etc., as used in the first layer.

A coating composition comprising pigment and about 3 to about 12 weight percent casein preferably about 6 to about 9 weight percent, based on total coating composition, can be employed. A casein to pigment ratio can be any ratio which gives a suitable density and desirable physical characteristics. Weight ratios of about 1:1 to about 8:1, preferably about 1.5:1 to about 3:1 can be used. These compositions are colored and give opaque backing layers comprising about 200 to about 1,200, preferably about 400 to about 800 mgs of casein per square foot and about 150 to about 400, preferably about 200 to about 300 mgs. of carbon per square foot.

A compatible polymeric film-forming material is also incorporated in the coating composition for either of the layers in amount of about 5 to 40 percent by weight of casein. Any film-forming polymer that has no detrimental effect on the photographic emulsion layer of the film and is compatible with casein and is not tacky after drying is suitable for being employed in the binder for either layer. Typically, water-insoluble polymers are used in latex form. Examples of suitable polymeric materials are for instance polyvinyl acetate, polystyrene, copolymers of styrene, copolymers of vinyl chloride, copolymers of vinylidene chloride, copolymers of alkylacrylates, etc. Particularly suitable examples are copolymers of styrene and butadiene such as Butakon SL 103 (trade name for an aqueous colloidal dispersion containing 46.4 percent of solids marketed by Imperial Chemical Industries Ltd., London SW. 1, England), Dow Latex (trade name for a series of latexes of styrene-butadiene copolymers comprising from 60 to 70 mole percent of styrene and from 46 to 48 percent by weight of solids marketed by the Dow Chemical Company, Midland, Mich., U.S.A.) such as Dow Latex 512R, Dow Latex 630 and Dow Latex 636, copolymers of vinyl chloride and butylacrylate such as Aeronal 350D (trade name of Badische Anilin- & Soda-Fabrik, Ludwigshafen (Rhine), (Germany) and copolymers of vinylidene chloride such as the Saran Latexes F 122-A 15 and F 122-A 20 (trade names of the Dow Chemical Company, Midland, Mich., U.S.A. for dispersions of vinylidene chloride-acrylonitrile copolymers in water comprising about 52% by weight of solids and about 15% by weight of dibutyl phthalate as plasticizer). Aqueous dispersions may be used of a water-insoluble linear polymer of monoethylenically unsaturated mole-

cules comprising a nitrogenous monomer having the general formula:



where R is H or CH₃, n is an integer having a value of 1 to 2, A is



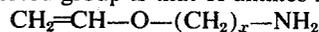
when n is 1 and selected from the group consisting of —O—,



and



when n is 2, R' is a straight or branched chain alkylene group having from two to 10 carbon atoms, and R², R³, and R₄ are each selected individually from the class consisting of H and saturated aliphatic hydrocarbon groups having from one to 10 carbon atoms. A preferred group is that of amines having the formula:



where x may be 2 to 10 but is preferably 2 to 5.

Examples of these monomers are:

Acrylamide

Methacrylamide

N-methyl methacrylamide

N-(γ-dimethylamino)propyl methacrylamide

N-(β-dimethylamino)ethyl acrylamide

N-(β-dimethylamino)ethyl methacrylamide

10-aminodecyl vinyl ether

8-aminooctyl vinyl ether

Diethylaminoethyl methacrylate

Diethylaminoethyl vinyl ether

5-aminopentyl vinyl ether

3-aminopropyl vinyl ether

2-aminoethyl vinyl ether

2-aminobutyl vinyl ether

4-aminobutyl vinyl ether

2-aminoethyl vinyl ether

Dimethylaminoethyl methacrylate

Dimethylaminoethyl vinyl ether

N-3,5,5-trimethylhexyl aminoethyl vinyl ether

N-cyclohexylaminoethyl vinyl ether

t-Butylaminoethyl acrylate

2-(1,1,3,3-tetramethylbutylamino)ethyl methacrylate

N-t-butylaminoethyl vinyl ether

N-methylaminoethyl vinyl ether

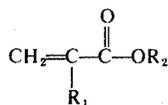
N-2-ethylhexylaminoethyl vinyl ether

N-t-octylaminoethyl vinyl ether

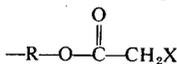
Particularly useful polymers are film-forming polymers containing at least about 0.1 percent, by weight, of active methylene groups in aliphatic side chains. A particularly effective class of interpolymers is prepared from acrylic type esters having active methylene groups in the ester moiety or in a substituent alpha to the car-

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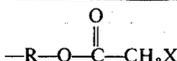
bonyl group. Such compounds can be represented by the formula:



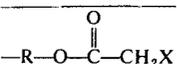
where R_1 is hydrogen, alkyl or



where R is alkylene and X is aliphatic acyl or cyano and R_2 is alkyl, cycloalkyl, aryl or



where R and X are as defined, provided that one and only one R_1 and R_2 is always



The ethylenically unsaturated polymerizable monomers having the above formula can be prepared using any procedure suitable for this purpose.

Typical polymers and suitable methods of preparation are disclosed in Smith U.S. Pat. No. 3,459,790 issued Aug. 5, 1969 and U.S. Pat. No. 3,488,708 issued Jan. 6, 1970.

The molecular weights of the film-forming polymers are subject to wide variation, but are often in the range of about 5,000 to about 500,000.

Film-forming polyethylene glycols which are useful in this invention are alkylene oxide polymers known also as polyglycols. A polyethylene glycol having an average molecular weight of about 4,000 is sold as Carbowax 4000 by Union Carbide Company. Other alkylene oxide polymers having molecular weights from 1,500 to 20,000 or greater can also be used. However, with the polyglycols having a high molecular weight, it may be desirable to add a small amount of low-weight glycol such as triethylene glycol as a plasticizer. The alkylene oxide polymers may be modified without destroying their usefulness for this process, provided that the modified material is compatible with useful proportions of water and of the processing chemicals. For example, mixed ethylene oxides and propylene oxide polymers may be employed, or derivatives such as esters, ethers, amides, etc. may also be used. A partial list of such derivatives is as follows:

- Oleic ester polyethylene oxide-1000;
- Nonylphenol ether polyethylene oxide-1145;
- N-methylmyristylamino polyethylene oxide-1045;
- Oleyl ether polyethylene oxide-1500;
- N-methyl-n-dodecylamino polyethylene oxide-1145;

Pluronic F38 (a polypropylene oxide-polyethylene oxide block polymer) sold by Wyandotte Chem. Corp.;

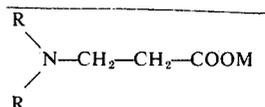
- Polyethoxyethyl-bis-sulfuric acid (M.W.=1500);
- Polyethoxyethyl-bis-carboglutamic acid (Na salt) (M.W.=1600)

Particularly useful film-forming materials which form an aqueous coating composition with casein, include,

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for example, copoly(butyl acrylate-sulfo propyl acrylate-2-aceto acetoxy ethyl methacrylate), polyvinyl acetate latex, polyethylene glycol, copolymer of n-butyl methacrylate and isobutyl methacrylate and copoly-
5 (ethyl acrylate-acrylic acid).

Coating aids are desirably included in casein-polymer coating compositions for example; saponin; and the like can be used. A particularly useful material, the N-alkyl-beta-amino-dipropionate has the following struc-
10 tural formula:



wherein R is an aliphatic hydrocarbon group containing 10-18 carbon atoms, R_1 is H, an aliphatic hydrocarbon group of 10-18 carbon atoms or $\text{CH}_2\text{CH}_2\text{COOM}$, and M is H or a salt-forming substituent such as an alkali metal, e.g., sodium, potassium or the like, or ammonium. Preferably, R and R_1 , when R_1 is alkyl, are aliphatic hydrocarbon atoms. N-alkyl-beta-aminodipropionate, alkali metal salt, wherein the alkyl group contains 12-18 carbon atoms, provides highly satisfactory results.

A product identified as N-tallow-beta-amino dipropionate is commercially available and is a mixture of N-alkyl-beta-aminodipropionates wherein the alkyl group has 10 to 18 carbon atoms.

Hardeners for casein which may be incorporated in the coating include dihydroxydioxane, formaldehyde, diacetal, chromic chloride, etc. Matting agents (which also serve to reduce friction) such as polymethylmethacrylate beads, silica, starch or glass particles, are often advantageously incorporated in the coatings of the invention. The quantity of these constituents in the compositions may be varied over a relatively wide range to obtain the desired results. We have found that amounts of hardener and matting agent of from 1-3 percent each, based on the dry weight of the casein, produce highly satisfactory results.

The coatings may be applied using various conventional coating methods such as a dip coater, brush coater, air brush coater (or air knife coater), extrusion, or hopper coater, or the like. Various temperatures may be used for coating, but a temperature somewhat above room temperature, about 80°F. is preferred. The flexible support may have a coating thereon in order to improve adhesion. For instance, the polyester support may have a sub layer on the surface prior to coating the opaque layer. The term "opaque" is intended to mean substantially impervious to visible light.

The opaque supports of this invention are advantageously used in image-receiving elements that are used to receive diffusion transfer images during the diffusion transfer process. At least one light sensitive silver salt is coated on the support, usually with the opaque coating on the other side. The receiving layer is also usually coated on an opaque support with the opaque coating on the other side. In these processes, a light-sensitive diffusion transfer element containing a light-image exposed silver halide emulsion is processed with the exposed emulsion layer in contact with the silver precipitating layer of an image-receiving element in the presence of a silver halide developing agent, such as hydroquinone, 1-phenyl-3-pyrazolidone, p-

methylaminophenol, etc., a silver halide solvent or complexing agent, such as an alkali metal thiosulfate, ammonium thiosulfate, etc., a thiocyanate such as an alkali metal thiocyanate, ammonium thiocyanate, etc. In a particularly useful process, a thickening agent, such as carboxymethylcellulose, carboxyethylcellulose, etc. is used.

During development, undeveloped silver halide forms a complex with the complexing agent which then diffuses in an imagewise manner to the silver-precipitating layer on the image-receiving element where a silver image is precipitated from the silver halide complex. In an integral element, a silver halide emulsion coated over a silver precipitating layer is removed such as by washing, to disclose the transferred image.

In a color diffusion transfer process, an image-exposed light-sensitive silver halide color diffusion transfer element is contacted with the receiving layer of an image-receiving element in the presence of a developer solution which causes the release of a diffusible dye image that transfers to the mordanted receiving layer. The desired dye image remains in the receiving layer when the receiving element is separated from the developed diffusion transfer element. The diffusible dye image is formed from an incorporated non-diffusible coupler that couples with an imagewise pattern of oxidized primary aromatic amine color developing agent, produced by development of light-exposed silver halide. In another system, the dye image is formed from incorporated dye developing agents, such as hydroquinone derivatives that contain a chromophore as a substituent; the hydroquinone form of these compounds forms in the alkaline developer solution a diffusible dye while the dye developer that is oxidized to the quinone form (when it develops light-exposed silver halide to silver) is insoluble and does not diffuse to the image-receiving layer.

The image-receiving elements comprise a support having the opaque coating on the back as described previously that has been coated on the face side with an image-receiving layer for a silver image comprising a silver precipitating agent or an image-receiving layer for a dye image comprising any suitable hydrophilic colloids containing a basic mordant for mordanting acid solubilized diffusible dyes.

Usually it is advantageous to have a hydrophobic resin layer between the support and the image-receiving layer. Hydrophobic resins that are advantageously used include poly(ethylene terephthalate), polyethylene, polypropylene, poly(3-methylbutene-1), poly(octene-1), poly(decene-1), polyamides, polyacetate, polycarbonates, cellulose triacetate, cellulose acetate butyrate, ethyl cellulose, etc.; preferably the hydrophobic resin layer is treated with corona discharge techniques just prior to coating the first hydrophilic colloid layer over the resin as described in U.S. Patents such as U.S. Pat. Nos. 3,220,842, 2,864,755, 2,864,756, etc.

Any suitable silver precipitant is advantageously used in the receiving layer. As examples of suitable silver precipitating agents and of image-receiving elements containing such silver precipitating agents, reference may be made to U.S. Pat. Nos. 2,698,237, 2,698,238 and 2,698,245, issued to Edwin H. Land on Dec. 28, 1954; U.S. Pat. No. 2,774,667, issued to Edwin H. Land and Meroe M. Morse on Dec. 18, 1956,

U.S. Pat. No. 3,396,018, issued to Beavers, et al., Aug. 6, 1968 and also U.S. Pat. No. 3,369,901, issued to Fogg, et al., Feb. 20, 1968. The noble metals, silver, gold, platinum, palladium, etc. in the colloidal form are particularly useful.

Noble metal nuclei are particularly active and useful when formed by reducing a noble metal salt using a borohydride or hypophosphite in the presence of a colloid. The metal nuclei are prepared in the presence of a colloid such as gelatin and coated on the receiving element. The coating composition generally contains not only nuclei, but also reaction products which are obtained from reducing the metal salt.

The amount of colloid used in preparing the above active noble metal nuclei can be varied depending upon the particular colloid, reducing agent, ratio of proportions, etc. Typically, about 0.5 percent to about 20 percent, by weight, based on the total reaction mixture of colloid is used, preferably from about 1 percent to about 10 percent.

In a particularly useful embodiment, 30 to 80 $\mu\text{g}/\text{ft}^2$ of the active noble metal nuclei in 80 mg of colloid (solids basis) is coated per square foot of support. The colloid binder is advantageously coated in a range of about 5 to about 500 mg/ft^2 . Suitable concentrations on the receiving sheets of active noble metal nuclei as disclosed above can be about 1 to about 200 $\mu\text{g}/\text{ft}^2$. Other silver precipitants can be coated in a concentration of up to 5 mg/ft^2 .

Any mordants that have a charge opposite to the charge of the dye being transferred are used to advantage in the image-receiving elements for dye transfer images. Since most of the useful photographic image-transfer dyes have acidic solubilizing groups, basic or cationic mordants are generally used. Typical mordants are organic quaternary phosphonium salts, organic ternary sulfonium salts and organic quaternary ammonium salts. Suitable mordants include polymers of amino guanidine derivatives of vinyl methyl ketone described in Minsk, U.S. Pat. No. 2,882,156. Other suitable mordants include the 2-vinyl pyridine polymer metho-p-toluene sulfonate, poly-4-vinyl pyridine, thorium salts and similar compounds described in Sprague, et al., U.S. Pat. No. 2,484,430.

A particularly useful class of mordanting compositions is disclosed in Bush, U.S. Pat. No. 3,271,147. Basic or cationic, nonpolymeric mordant compounds of Bush include quaternary ammonium and phosphonium, and tertiary sulfonic compositions in which there is linked to the N, P or S onium atom at least one hydrophobic ballast group, such as long-chain alkyl or substituted alkyl groups. The onium atom can be part of an open-chain or of a heterocyclic ring and there can be more than one onium ring in the molecule. When referring to the nonpolymeric nature of the mordant compounds of such mordanting compositions, it is understood that the cationic or the basic mordant does not have regularly occurring units containing the cationic group beyond the dimer structures. However, the ballast group attached to the quaternary or tertiary atom of the cation group can contain repeating groups such as tetra-ethoxy, polymethylene, etc.

The following examples are included for a further understanding of the invention.

EXAMPLES

Several film bases are prepared as follows. Each has

an opaque layer and a contiguous overcoat layer coated on a polyethylene terephthalate film support. Each coating is then tested for crack resistance by passing it at right angles over a rounded edge of short radius. Identification and cracking evaluation is summarized in Table I.

as the silver salt diffusion transfer system described in Land U.S. Pat. No. 2,543,181, issued Feb. 27, 1951. The opaque backing layers on polyester support showed little "white light print through".

The silver halide emulsions used which can be coated on the supports of this invention can comprise silver

TABLE I

	Opaque Layer A	Coverage mg/ft ²	Overcoat Layer B	Coverage mg/ft ²	Cracking Evaluation
1 (Control)	Casein	632	Casein	56.5	1
	Carbon Black	266	Polymethylmethacrylate beads	5.2	
	2,3-dihydroxy-1,4-dioxane	50	N-stearoyl-β-imino dipropionate	6.0	
	Saponin	4.8	2,3-dihydroxy-1,4-dioxane Saponin	4.5	
2	As (1) above + Polymer A	126	As (1) above + Polymer A	11	2
3	As (1) above + Polymer B	158	As (1) above + Polymer B	14	2
4	As (1) above + Polymer C	31	As (1) above + Polymer C	2.8	3
5	As (1) above + Polymer D	110	As (1) above + Polymer D	8.5	3
6	Casein	254	As (1) above + colloidal silica ²	5.6	3
	Carbon black	266			
	Colloidal silica ⁴	45	Polyacrylamide	5.6	
	Polyacrylamide	45			
	Mucochloric acid	1.2			

Polymer A = Copoly(butyl acrylate-sulfopropyl acrylate-2-aceto-acetoxyethyl methacrylate)

Polymer B = Polyvinyl acetate latex with 10 percent dibutyl phthalate as a plasticizer

Polymer C = Polyethylene glycol having a molecular weight of 4,000 (Carbowax 4000)

Polymer D = Copolymer of n-butyl and isobutyl methacrylate

Samples of the above polyethylene terephthalate supports bearing the various backing layers are also coated on the opposite side as a dye developer transfer element such as described in Example 1 of Weyerts et al. U.S. Pat. No. 3,146,102. The above polyethylene terephthalate bases are represented by Support 10 of Example 1 of Weyerts et al. Samples of the resultant elements are exposed, passed at right angles over a rounded edge of short radius, wetted with activators, brought into contact with a receiver sheet and processed in white light as described in Example 1 of U.S. Pat. No. 3,146,102. Results show visible "white light print through" (i.e., undesirable fogged images corresponding to the cracking of the opaque layer) in Coating 1 above while the others showed little or no "print through" defects.

Samples of the above polyethylene terephthalate having opaque backing layers according to this invention are coated on the opposite side with a silver chlorobromide emulsion and used in a photographic transfer system designed for "white light" processing such

chloride, silver bromide, silver iodide, silver bromoiodide, silver chloroiodide, silver chlorobromide, silver chlorobromoiodide or mixtures thereof. The emulsions may be coarse or fine grain and can be prepared by any of the well-known procedures, e.g., single jet emulsions, double jet emulsions, such as Lippmann emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions such as those described in Nietz et al. U.S. Pat. No. 2,222,264; Illingsworth U.S. Pat. No. 3,320,069; and McBride U.S. Pat. No. 3,271,157. Surface image emulsions may be used or internal image emulsions such as those described in Davey et al. U.S. Pat. No. 2,592,250; Porter et al. U.S. Pat. No. 3,206,313; Berriman U.S. Pat. No. 3,367,778 and Bacon et al. U.S. Pat. No. 3,447,927. If desired, mixtures of surface and internal image emulsions may be used as described in Luckey et al. U.S. Pat. No. 2,996,382. The emulsions may be regular grain emulsions such as the type described in Klein and Moisar, J. Phot. Sci., Vol. 12, No. 5, Sept./Oct., 1964, pp. 242-251.

The emulsions may be sensitized with chemical sensitizers, such as with reducing agents; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Suitable procedures are described in Sheppard et al. U.S. Pat. No. 1,623,499; Waller et al. U.S. Pat. No. 2,399,083; McVeigh U.S. Pat. No. 3,297,447; and Dunn U.S. Pat. No. 3,297,446.

The emulsions can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers each used alone or in combination include thiazolium salts described in Brooker et al. U.S. Pat. No. 2,131,038 and Allen et al. U.S. Pat. No. 2,694,716; the azaindenes described in Piper U.S. Pat. No. 2,886,437 and Heimbach et al. U.S. Pat. No. 2,444,605; the mercury salts as described in Allen et al. U.S. Pat. No. 2,728,663; the urazoles described in Anderson et al. U.S. Pat. No. 3,287,135; the sulfocatechols described in Kennard et al. U.S. Pat. No. 3,236,652; the oximes described in Carroll et al. British Patent 623,448; nitron; nitroindazoles; the mercaptotetrazoles described in Kendall et al. U.S. Pat. No. 2,403,927; Kennard et al. U.S. Pat. No. 3,226,897 and Luckey et al. U.S. Pat. No. 3,397,987; the polyvalent metal salts described in Jones U.S. Pat. No. 2,839,405; the palladium, platinum and gold salts described in Trivelli et al. U.S. Pat. No. 2,566,263 and Yutzy et al. U.S. Pat. No. 2,597,915.

The photographic and other hardenable layers used can be hardened by various organic or inorganic hardeners, alone or in combination, such as the aldehydes, and blocked aldehydes, ketones, carboxylic and carbonic acid derivatives, sulfonate esters sulfonyl halides and vinyl sulfonyl ethers, active halogen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodiimides, mixed function hardeners and polymeric hardeners such as oxidized polysaccharides, e.g., dialdehyde starch, oxyguargum and the like.

The photographic emulsions and elements can contain various colloids alone or in combination as vehicles, binding agents and various layers. Suitable hydrophilic materials include both naturally-occurring substances such as proteins, for example, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water soluble polyvinyl compounds like poly(vinylpyrrolidone), acrylamide polymers and the like.

The photographic elements used may contain antistatic or conducting layers; such layers may comprise soluble salts, e.g., chlorides; nitrates, etc., evaporated metal layers, ionic polymers such as those described in Minsk U.S. Pat. No. 2,861,056 and Serman et al. U.S. Pat. No. 3,206,312 or insoluble inorganic salts such as those described in Trevoys U.S. Pat. No. 3,428,451.

The photographic layers can contain plasticizers and lubricants such as polyalcohols, e.g., glycerin and diols of the type described in Milton et al. U.S. Pat. No. 2,960,404; fatty acids or esters such as those described in Robijns U.S. Pat. No. 2,588,765 and Duane U.S. Pat. No. 3,121,060; and silicone resins such as those described in DuPont British Patent 955,061.

The photographic layers may contain surfactants such as saponin, anionic compounds such as the alkyl aryl sulfonates described in Baldsiefen U.S. Pat. No. 2,600,831; amphoteric compounds such as those described in Ben-Ezra U.S. Pat. No. 3,133,816; and water soluble adducts of glycidol and an alkyl phenol such as those described in Olin Mathieson British Patent 1,022,878.

The photographic elements may contain matting agents such as starch, titanium dioxide, zinc oxide, silica, polymeric beads including beads of the type described in Jelley et al. U.S. Pat. No. 2,992,101 and

Lynn U.S. Pat. No. 2,701,245.

The photographic elements contain brightening agents including stilbenes, triazines, oxazoles and coumarin brightening agents. Water soluble brightening agents may be used such as those described in Albers et al. German Patent 972,067 and McFall et al. U.S. Pat. No. 2,933,390 or dispersions of brighteners may be used such as those described in Jansen German Patent 1,150,274, Oetiker et al. U.S. Pat. No. 3,406,070 and Heidke French Patent 1,530,244.

Spectral sensitizing dyes can be used conveniently to confer additional sensitivity to the light sensitive silver halide emulsion of the multilayer photographic elements. For instance, additional spectral sensitization can be obtained by treating the emulsion with a solution of a sensitizing dye in an organic solvent or the dye may be added in the form of a dispersion as described in Owens et al. British Patent 1,154,781. For optimum results, the dye may either be added to the emulsion as a final step or at some earlier stage.

Sensitizing dyes useful in sensitizing such emulsions are described, for example, in Brooker et al. U.S. Pat. No. 2,526,632, issued Oct. 24, 1950; Sprague U.S. Pat. No. 2,503,776, issued Apr. 11, 1950; Brooker et al. U.S. Pat. No. 2,493,748; and Tabor et al. U.S. Pat. No. 3,384,486. Spectral sensitizers which can be used include the cyanines, merocyanines, complex (tri or tetranuclear) merocyanines, complex (tri or tetranuclear) cyanines, holopolar cyanines, styryls, hemicyanines (e.g., enamine hemicyanines), oxonols and hemioxonols.

The various layers, including the photographic layers, can contain light absorbing materials and filter dyes such as those described in Sawdey U.S. Pat. No. 3,253,921; Gaspar U.S. Pat. No. 2,274,782; Silberstein et al. U.S. Pat. No. 2,527,583 and VanCampen U.S. Pat. No. 2,956,879. If desired, the dyes can be mordanted, for example, as described in Jones et al. U.S. Pat. No. 3,282,699.

The photographic layers may be coated by various coating procedures including dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in Beguin U.S. Pat. No. 2,681,294. If desired, two or more layers may be coated simultaneously by the procedures described in Russell U.S. Pat. No. 2,761,791 and Wynn British Patent 837,095.

This invention may be used with elements designed for color photography, for example, elements containing color-forming couplers such as those described in Frohlich, et al. U.S. Pat. No. 2,376,679, Jelley et al. U.S. Pat. No. 2,322,027, Fierke et al. U.S. Pat. No. 2,801,171, Godowsky U.S. Pat. No. 2,698,794, Barr et al. U.S. Pat. No. 3,227,554 and Graham et al. U.S. Pat. No. 3,046,129; or elements to be developed in solutions containing color-forming couplers such as those described in Mannes et al. U.S. Pat. No. 2,252,718, Carroll et al. U.S. Pat. No. 2,592,243 and Schwan et al. U.S. Pat. No. 2,950,970; and in false-sensitized color materials such as those described in Hanson U.S. Pat. No. 2,763,549.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. An element comprising a flexible support having on one side an opaque coating comprising a first opaque layer having a binder comprising casein, an opaquing pigment and a compatible film-forming organic polymeric material and a second layer contiguous thereto having a binder comprising casein and a compatible film-forming organic polymeric material only one of said layers containing an opaquing pigment and having on the other side a silver halide emulsion.

2. An opaque element of claim 1 in which said polymeric material comprises a polymeric latex.

3. An element of claim 1 in which said polymeric material in at least one layer comprises polyacrylamide.

4. An element of claim 1 in which at least one layer comprises n-alkyl-β-amino dipropionate.

5. An element of claim 1 in which said second layer comprises polyethyl methacrylate beads.

6. An element of claim 1 in which said polymeric material in at least one layer comprises copoly(butyl acrylate-sulfopropyl acrylate-2-acetoacetoxyethyl methacrylate).

7. An element of claim 1 in which said polymeric material in at least one layer comprises polyvinyl acetate.

8. An element of claim 1 in which said polymeric material in at least one layer comprises polyethylene glycol.

9. An element of claim 1 in which said polymeric material in at least one layer comprises a copolymer of n-butyl and isobutyl methacrylate.

10. An element of claim 1 in which said polymeric material in at least one layer comprises copoly(ethylacrylate-acrylic acid).

11. An element of claim 1 in which each said layer comprises about 200 to about 1,200 mgs of casein per square foot.

12. An element of claim 1 in which said first layer comprises about 150 to about 400 mgs. of carbon per square foot.

13. An element of claim 1 in which said layers comprise about 5 to about 40% by weight of said film-forming polymer based on said casein.

14. An element of claim 1 in which said support is a polyester.

15. An element of claim 1 in which said support is polyethylene terephthalate.

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