United States Patent [19]

Liang

[11] **3,784,382**

[45] **Jan. 8, 1974**

[54] **INTERNAL SUPPORT FOR DIFFUSION TRANSFER ELEMENT**

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[22] Filed: **Jan. 3, 1972**

[21] Appl. No.: **215,096**

[52] **U.S. Cl.** ..... **96/77,** 96/3, 96/29 D, 96/76 C

[51] **Int. Cl.** **G03c 1/76,** G03c 5/54, G03c 7/00

[58] **Field of Search** ..... 96/3, 29 D, 77, 83, 96/95, 76 C, 29 R

[56] **References Cited**

OTHER PUBLICATIONS

General Electric; Research Laboratory Bulletin; Winter 1964–1965; pages 12–14.

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[57] **ABSTRACT**

An internal support for a photographic element and film unit is described comprising a porous, polymeric material with pore diameters ranging from about 0.5 to about 12 microns and a porosity of from about 1 to about 25 percent. The transfer image has an improved image quality and sharpness and postprocess retention of processing fluid is minimized.

11 Claims, No Drawings

INTERNAL SUPPORT FOR DIFFUSION TRANSFER ELEMENT

This invention relates to the art of photography and more particularly to color diffusion transfer film systems and photosensitive elements having increased image sharpness.

U.S. Pat. Nos. 2,500,421 issued Mar. 14, 1950, and 3,573,044 issued Mar. 30, 1971, disclose the use of permeable supports in image transfer systems. The use of the particular porous polymeric material of the instant invention is not disclosed in these patents, however, nor is the internal location of the porous support disclosed which is an important feature of this invention.

It is an object of this invention to provide diffusion transfer reflection prints and transparencies having an improved image quality and sharpness.

It is another object of this invention to provide photographic elements and film units having an internal porous polymeric support wherein the postprocess retention of processing fluid is minimized.

These and other objects are achieved by my invention which is described hereinafter.

A photographic element according to my invention comprises a support having thereon a dye image-receiving layer, a substantially opaque, light-reflective layer, and at least one photosensitive silver halide emulsion layer having a dye image-providing material associated therewith capable of reacting with oxidized developing agent to produce a dye, wherein:

a. said support is a porous, polymeric material with pore diameters ranging from about 0.5 to about 12 microns and a porosity of from about 1 to about 25 percent, and

b. all of said layers are not located on the same side of the support.

One example of a porous polymeric support as described above is marketed by General Electric Company under the trademark "Nuclepore." This material is made from a hydrophilic polycarbonate and has a range of available pore diameters of from about 0.5 to about 12 microns. The available pore densities range from 1×10^3 to 1×10^9 pores per square centimeter, or from about 1 to about 25 percent open porosity. This material has straight-through pores which are made by exposing it to charged particle bombardment in a nuclear reactor followed by chemical etching. The thickness of the material is about 10 to about 12 microns and is stable at high pH's. Dyes or pigments can also be added to the polymer to provide various colors, e.g., white for a light-reflective layer or black for an opaque layer. Although polycarbonates are preferred, glass, silicon and polyesters can also be made porous in a similar fashion.

The above-described photographic element is especially useful in photographic film units wherein the image-receiving layer is integral with the photosensitive layers and no stripping of an image-receiving element from the negative is required. These film units are well-known in the art as illustrated, for example, by U.S. Pat. Nos. 3,415,644, 3,415,645 and 3,415,646, all issued Dec. 10, 1968, and Belgian Pat. Nos. 757,959 and 757,960, both issued Apr. 23, 1971.

In a highly preferred embodiment, a photographic film unit according to my invention which is adapted to be processed by passing the unit between a pair of juxtaposed pressure-applying members comprises:

I. a photosensitive element as described above;

II. a transparent sheet superposed over the silver halide emulsion layer of the photosensitive element; and

III. a rupturable container containing alkaline processing composition having therein an opacifying agent, the rupturable container being positioned transverse a leading edge of the photosensitive element so that a compressive force applied to the container by the pressure-applying members will effect a discharge of the container's contents between the transparent sheet and the underlying silver halide emulsion layer of the photosensitive element adjacent thereto.

As mentioned above, the internal location of the porous polymeric support is an important feature of my invention. All of the layers described above are not located on one side of the support in order to take advantage of the desirable properties of the support. The porous support described above can be employed in an integral film unit above, below or combined with a white light-reflective layer or an opaque carbon black layer. In addition, the porous support can also be located between the various silver halide emulsion layers of the photosensitive element. In a highly preferred embodiment, the dye image-receiving layer and light-reflective layer are located on one side of the support and the photosensitive layer of layers are located on the other side of the support. In this embodiment, the natural tendency of soluble image dyes to travel in a diffused pattern from their points of origin in the emulsion layer to the dye image-receiving layer will be minimized. Since the dyes travel through the porous support which contains straight-through pores, the dyes reach the dye image-receiving layer with a minimum of lateral diffusion, thereby producing an image having greater sharpness. Improved sharpness is an especially desirable property in a transparency since distortions in the image pattern of diffused dyes when magnified on a screen are very noticeable. In addition, such an image will dry much faster since processing liquid will not be permanently trapped between two water-impermeable supports, as is the case in some integral systems. Having water present in an integral film unit after processing is usually undesirable since additional unwanted dye producted in the negative will continue to transfer to the dye image-receiving layer via the water medium. In my system, the film unit will dry rapidly since water is readily transmitted through the porous support, thus obviating a deterioration of the dye image.

In the embodiment described above, the dye image-receiving layer can be overcoated with an antiabrasion overcoat, well-known to those skilled in the art, in order to protect the image from being distorted by handling. It is to be noted that the drying mechanism described above is not the same as in a peel-apart system. A peel-apart print has the processing liquid on the top for drying as opposed to the integral system where the processing liquid is internal and has to diffuse to the dye image-receiving element, with water ultimately escaping through the vapor-permeable top layer.

The film unit of my invention can be used to produce positive or negative images in single- or multicolors. In a three-color system, each silver halide emulsion layer of the film unit of my invention will have associated

therewith a dye image-providing material possessing a spectral absorption range substantially complementary to the predominant sensitivity range of its associated emulsion, i.e., the blue-sensitive silver halide emulsion layer will have a yellow dye image-providing material associated therewith, the green-sensitive silver halide emulsion layer will have a magenta dye image-providing material associated therewith, and the red-sensitive silver halide emulsion layer will have a cyan dye image-providing material associated therewith. The dye image-providing material associated with each silver halide emulsion layer can be contained either in the silver halide emulsion layer itself or in a layer contiguous to the silver halide emulsion layer.

Spectral sensitizing dyes can be used conveniently to confer additional sensitivity to the light sensitive silver halide emulsion of the multilayer photographic elements of the invention. 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 Pat. No. 1,154,781 issued June 11, 1969. For optimum results, the dye can 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, issued Jan. 10, 1950; and Taber et al., U.S. Pat. No. 3,384,486 issued May 21, 1968. 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. Dyes of the cyanine classes can contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazoles, thiazoles, selenazoles and imidazoles. Such nuclei can contain alkyl, alkylene, hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminoalkyl and enamine groups and can be fused to carbocyclic or heterocyclic ring systems either unsubstituted or substituted with halogen, phenyl, alkyl, haloalkyl, cyano, or alkoxy groups. The dyes can be symmetrical or unsymmetrical and can contain alkyl, phenyl, enamine or heterocyclic substituents on the methine or polymethine chain. The merocyanine dyes can contain the basic nuclei mentioned above as well as acid nuclei such as thiohydantoins, rhodanines, oxazolidenediones, thiazolidenediones, barbituric acids, thiazolineones, and malononitrile. These acid nuclei can be substituted with alkyl, alkylene, phenyl, carboxyalkyl, sulfoalkyl, hydroxyalkyl, alkoxyalkyl, alkylamino groups, or heterocyclic nuclei. Combinations of these dyes can be used, if desired. In addition, supersensitizing addenda which do not absorb visible light can be included, for instance, ascorbic acid derivatives, azaindenes, cadmium salts, and organic sulfonic acids as described in McFall et al., U.S. Pat. No. 2,933,390 issued Apr. 19, 1960 and Jones et al., U.S. Pat. No. 2,937,089 issued May 17, 1960.

The various silver halide emulsion layers of a color film assembly of the invention can be disposed in the usual order, i.e., the blue-sensitive silver halide emulsion layer first with respect to the exposure side, followed by the green-sensitive and red-sensitive silver halide emulsion layers. If desired, a yellow dye layer or a Carey Lea silver layer can be present between the blue-sensitive and green-sensitive silver halide emulsion layer for absorbing or filtering blue radiation that may be transmitted through the blue-sensitive layer. If desired, the selectively sensitized silver halide emulsion layers can be disposed in a different order, e.g., the blue-sensitive layer first with respect to the exposure side, followed by the red-sensitive and green-sensitive layers.

The silver halide emulsions used in this invention can comprise, for example, silver chloride, silver bromide, silver chlorobromide, silver bromoidide, silver chlorobromoiodide or mixtures thereof. The emulsions can be coarse or fine grain and can be prepared by any of the well-known procedures, e.g., single jet emulsions such as those described in Trivelli and Smith, *The Photographic Journal*, Vol. LXXIX, May, 1939 (pp 330–338), 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 issued Nov. 19, 1940; Illingsworth U.S. Pat. No. 3,320,069 issued May 16, 1967; and McBride U.S. Pat. No. 3,271,157 issued Sept. 6, 1966. Surface image emulsions can be used or internal image emulsions can be used such as those described in Davey et al., U.S. Pat. No. 2,592,250 issued May 8, 1952; Porter et al., U.S. Pat. No. 3,206,313 issued Sept. 14, 1965; Berriman U.S. Pat. No. 3,367,778 issued Feb. 6, 1968; and Bacon et al., U.S. Pat. No. 3,447,927 issued June 3, 1969. 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). Negative type emulsions may be used or direct positive emulsions may be used such as those described in Leermakers U.S. Pat. No. 2,184,013 issued Dec. 19, 1939; Kendall et al., U.S. Pat. No. 2,541,472 issued Feb. 13, 1951; Berriman U.S. Pat. No. 3,367,778 issued Feb. 6, 1968; Schouwenaars British Pat. No. 723,019 issued Feb. 2, 1955; Illingsworth et al., French Pat. No. 1,520,821 issued Mar. 4, 1968; Illingsworth U.S. Pat. No. 3,501,307 issued Mar. 17, 1970; Ives U.S. Pat. No. 2,563,785 issued Aug. 7, 1951; Knott et al., U.S. Pat. No. 2,456,953 issued Dec. 21, 1948; and Land U.S. Pat. No. 2,861,885 issued Nov. 25, 1958.

The emulsions used with this invention 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 issued Apr. 5, 1927; Waller et al., U.S. Pat. No. 2,399,083 issued Apr. 23, 1946; McVeigh U.S. Pat. No. 3,297,447 issued Jan. 10, 1967; and Dunn U.S. Pat. No. 3,297,446 issued Jan. 10, 1967.

The silver halide emulsions used with this invention may contain speed increasing compounds such as polyalkylene glycols, cationic surface active agents and thioethers or combinations of these as described in Piper U.S. Pat. No. 2,886,437 issued May 12, 1959; Dann et al., U.S. Pat. No. 3,046,134 issued July 24, 1962; Carroll et al., U.S. Pat. No. 2,944,900 issued July 12, 1960; and Goffe U.S. Pat. No. 3,294,540 issued Dec. 27, 1966.

The silver halide emulsions used in the practice of this invention 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 issued Sept. 27, 1938; and Allen et al., U.S. Pat. No. 2,694,716 issued Nov. 16, 1954; the azaindenes described in Piper U.S. Pat. No. 2,886,437 issued May 12, 1959; and Heimbach et al., U.S. Pat. No. 2,444,605 issued July 6, 1948; the mercury salts as described in Allen et al., U.S. Pat. No. 2,728,663 issued Dec. 27, 1955; the urazoles described in Anderson et al., U.S. Pat. No. 3,287,135 issued Nov. 22, 1966; the sulfocatechols described in Kennard et al. U.S. Pat. No. 3,236,652 issued Feb. 22, 1966; the oximes described in Carroll et al., British Pat. No. 623,448 issued May 18, 1949; nitron; nitroindazoles; the mercaptotetrazoles described in Kendall et al., U.S. Pat. No. 2,403,927 issued July 16, 1946; Kennard et al., U.S. Pat. No. 3,266,897 issued Aug. 16, 1966; and Luckey et al., U.S. Pat. No. 3,397,987 issued Aug. 20, 1968; the polyvalent metal salts described in Jones U.S. Pat. No. 2,839,405 issued June 17, 1958; the thiuronium salts described in Herz et al. U.S. Pat. No. 3,220,839 issued Nov. 30, 1965; the palladium, platinum and gold salts described in Trivelli et al U.S. Pat. No. 2,566,263 issued Aug. 28, 1951; and Yutzy et al., U.S. Pat. No. 2,597,915 issued May 27, 1952; and the tetrazoles described in Hoppe U.S. Pat. No. 3,352,672 issued Nov. 14, 1967.

Any dye image-providing material can be employed in this invention as long as an imagewise distribution of the material will be formed after development as a function of the imagewise exposure of the silver halide emulsion to which the dye image-providing material is associated. For example, there may be employed as the dye image-providing material dye developers as illustrated by U.S. Pat. No. 2,983,606; coupling dyes as disclosed, for example, in U.S. Pat. No. 3,087,817; "shifted" or "leuco" dye developers; dye developer precursors; metal dye complexes as disclosed, for example, in U.S. Pat. Nos. 3,185,567 and 3,453,107; couplers requiring an oxidizing agent in the image-receiving layer to form a color; "ring-closing" dye developers as disclosed in U.S. Pat. No. 3,443,943; color-providing materials as disclosed in U.S. Pat. No. 3,443,940 and 3,443,941; nondiffusible couplers which produce a diffusible dye upon reaction with oxidized aromatic primary amino color developing agents, such as p-phenylenediamine developing agents, as disclosed in U.S. Pat. Nos. 3,227,550, 3,227,551, 3,227,552, etc.

If the silver halide emulsion employed with the nondiffusible couplers described above is a direct positive silver halide emulsion, such as an internal image emulsion or a solarizing emulsion, which is developable in unexposed areas, a positive image can be obtained on the dye image-receiving layer. In this embodiment, the nondiffusible coupler can be located in the silver halide emulsion itself. After exposure of the film unit, the alkaline processing composition permeates the various layers to initiate development of the exposed photosensitive silver halide emulsion layers. The aromatic primary amino color developing agent present in the film unit develops each of the silver halide emulsion layers in the unexposed areas (since the silver halide emulsions are direct positive ones), thus causing the developing agent to become oxidized imagewise corresponding to the unexposed areas of the direct positive silver halide emulsion layer. The oxidized developing agent then reacts with the nondiffusible coupler present in each silver halide emulsion layer to form imagewise distributions, respectively, of diffusible cyan, magenta and yellow dye as a function of the imagewise exposure of each of the silver halide emulsion layers. At least a portion of the imagewise distributions of diffusible cyan, magenta and yellow dye diffuse to the image-receiving layer to provide a positive dye image.

Internal image silver halide emulsions useful in the above-described embodiment are direct positive emulsions that form latent images predominantly inside the silver halide grains, as distinguished from silver halide grains that form latent images predominantly on the surface thereof. Such internal image emulsions were described by Davey et al., in U.S. Pat. No. 2,592,250 issued Apr. 8, 1952, and elsewhere in the literature. These emulsions can also contain fogging or nucleating agents such as those described in U.S. Pat. Nos. 2,588,982; 2,563,785; 3,227,552; etc.

In a color film unit according to the invention, each silver halide emulsion layer containing a dye image-providing material or having the dye image-providing material present in a contiguous layer may be separated from the other silver halide emulsion layers in the negative portion of the film unit by materials in addition to those described above, including gelatin, calcium alginate, or any of those disclosed in U.S. Pat. No. 3,384,483, polymeric materials such as polyvinylamides as disclosed in U.S. Pat. No. 3,421,892, or any of those disclosed in U.S. Pat. Nos. 2,992,104; 3,043,692; 3,044,873; 3,061,428; 3,069,263; 3,069,264; 3,121,011; and 3,427,158.

Generally speaking, except where noted otherwise, the silver halide emulsion layers in the invention comprise photosensitive silver halide dispersed in gelatin and are about 0.6 to 6 microns in thickness; the dye image-providing materials are dispersed in an aqueous alkaline solution-permeable polymeric binder, such as gelatin, as a separate layer about 1 to 7 microns in thickness; and the alkaline solution-permeable polymeric interlayers, e.g., gelatin, are about 1 to 5 microns in thickness. Of course, these thicknesses are approximate only and can be modified according to the product desired. In addition to gelatin, other suitable hydrophilic materials include both naturally-occurring substances such as proteins, 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 emulsion layers and other layers of a photographic element employed in the practice of this invention can also contain alone or in combination with hydrophilic, water-permeable colloids, other synthetic polymeric compounds such as dispersed vinyl compounds such as in latex form and particularly those which increase the dimensional stability of the photographic materials. Suitable synthetic polymers include those described, for example, in Nottorf U.S. Pat. No. 3,142,568, issued July 28, 1964; White U.S. Pat. No. 3,193,386, issued July 6, 1965; Houck et al. U.S. Pat. No. 3,062,674, issued Nov. 6, 1962; Houck et al. U.S. Pat. No. 3,220,844, issued Nov. 30, 1965; Ream et al., U.S. Pat. No. 3,287,289, issued Nov. 22, 1966; and Dykstra U.S. Pat. No. 3,411,911, issued Nov. 19, 1968. Particularly effective are water-insoluble polymers of

alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, those which have cross-linking sites which facilitate hardening or curing described in Smith U.S. Pat. No. 3,488,708 issued Jan. 6, 1970, and those having recurring sulfobetaine units as described in Dykstra Canadian Pat. No. 774,054.

Any material can be employed as the image-receiving layer in this invention as long as the desired function of mordanting or otherwise fixing the dye images will be obtained. The particular material chosen will, of course, depend upon the dye to be mordanted. If acid dyes are to be mordanted, the image-receiving layer can contain basic polymeric mordants such as polymers of amino guanidine derivatives of vinyl methyl ketone such as described in Minsk U.S. Pat. No. 2,882,156 issued Apr. 14, 1959, and basic polymeric mordants such as described in Cohen et al U.S. Pat. No. 3,709,690, issued Jan. 9, 1973. Other mordants useful in this invention include poly-4-vinylpyridine, the 2-vinyl pyridine polymer metho-p-toluene sulfonate and similar compounds described in Sprague et al U.S. Pat. No. 2,484,430 issued Oct. 11, 1949, and cetyl trimethylammonium bromide, etc. Effective mordanting compositions are also described in Whitmore U.S. Pat. No. 3,271,148 and Bush U.S. Pat. No. 3,271,147, both issued Sept. 6, 1966.

Furthermore, the image-receiving layer can be sufficient by itself to mordant the dye as in the case of use of an alkaline solution-permeable polymeric layer such as N-methoxy-methyl polyhexylmethylene adipamide; partially hydrolyzed polyvinyl acetate; polyvinyl alcohol with or without plasticizers; cellulose acetate; gelatin; and other materials of a similar nature. Generally, good results are obtained when the image-receiving layer, preferably alkaline solution-permeable, is transparent and about 0.25 to about 0.04 mil in thickness. This thickness, of course, can be modified depending upon the result desired. The image-receiving layer can also contain ultraviolet absorbing materials to protect the mordanted dye images from fading due to ultraviolet light, brightening agents such as the stilbenes, coumarins, triazines, oxazoles, dye stabilizers such as the chromanols, alkylphenols, etc.

Use of a pH-lowering material associated with the dye image-receiving layer of the invention will usually increase the stability of the transferred image. Generally, the pH-lowering material will effect a reduction in the pH of the image layer from about 13 or 14 to at least 11 and preferably 5–8 within a short time after imbibition. For example, polymeric acids as disclosed in U.S. Pat. No. 3,362,819; or metallic salts, e.g., zinc acetate, zinc sulfate, magnesium acetate, the formates, acetates, propionates, stearates, nitrates, or sulfates of zinc, aluminum, iron, manganese, cobalt of nickel, etc.; or solid acids as disclosed in U.S. Pat. No. 2,584,030 may be employed with good results. Such pH-lowering materials reduce the pH of the film unit after development to terminate development and substantially reduce further dye transfer and thus stabilize the dye image. The pH-lowering material can be located between the light-reflecting layer and the lowermost silver halide emulsion layer in an integral receiver-negative element.

Any opacifying agent can be employed in the light-reflecting layer according to this invention. Particularly desirable are white opacifying agents since they would provide an esthetically pleasing background on which to view a transferred dye image and would possess the optical properties desired for reflection of incident radiation. Suitable opacifying agents include: titanium dioxide, barium sulfate, zinc oxide, barium stearate, silver flake, silicates, alumina, zirconium oxide, zirconium acetyl acetate, sodium zirconium sulfate, kaolin, mica, or mixtures thereof in widely varying amounts depending upon the degree of opacity desired. Especially good results are obtained with titanium dioxide. Zinc oxide in combination with titanium dioxide may also be employed to great advantage as disclosed and claimed in copending application Ser. No. 174,443 of Abbott, Dappen and Irani filed Aug. 24, 1971. Brightening agents such as the stilbenes, coumarins, triazines and oxazoles can also be added to the opacifying layer if desired.

The alkaline processing composition employed in this invention is the conventional aqueous solution of an alkaline material, e.g., sodium hydroxide, sodium carbonate or an amine such as diethylamine, preferably possessing a pH in excess of 12. The solution also preferably contains a viscosity-increasing compound such as a high molecular weight polymer, e.g., a water-soluble ether inert to alkaline solutions such as hydroxyethyl cellulose or alkali metal salts of carboxymethyl cellulose such as sodium carboxymethyl cellulose. A concentration of viscosity-increasing compound of about 1 to about 5 percent by weight of the processing solution is preferred which will impart thereto a viscosity of about 100 cps. to about 200,000 cps.

While the alkaline processing composition used in this invention can be employed in a rupturable container, other methods of applying processing composition could also be employed, e.g., bathing the photosensitive element in a processing bath, interjecting processing composition with communicating members similar to hypodermic syringes which are attached either to a camera or camera cartridge, etc.

While the film units of my invention can be modified so as to be employed in roll form, they are preferably used in cartridges similar to those described in U.S. Pat. Nos. 3,080,805; 3,161,118; and 3,161,122; said patents also illustrating typical cameras for performing color diffusion transfer processes of my invention.

The photographic layers employed in the practice of this invention may contain surfactants such as saponin; anionic compounds such as the alkyl aryl sulfonates described in Baldsiefen U.S. Pat. No. 2,600,831 issued June 17, 1952; amphoteric compounds such as those described in Ben-Ezra U.S. Pat. No. 3,133,816 issued May 19, 1964; and water soluble adducts of glycidol and an alkyl phenol such as those described in Olin Mathieson British Pat. No. 1,022,878 issued Mar. 16, 1966; and Knox U.S. Pat. No. 3,514,293 issued May 26, 1970.

The various layers, including the photographic layers, employed in the practice of this invention can contain light absorbing materials and filter dyes such as those described in Sawdey U.S. Pat. No. 3,253,921 issued May 31, 1966; Gaspar U.S. Pat. No. 2,274,782 issued Mar. 3, 1942; Silverstein et al., U.S. Pat. No. 2,527,583 issued Oct. 31, 1950; and VanCampen U.S. Pat. No. 2,956,879 issued Oct. 18, 1960.

The sensitizing dyes and other addenda used in the practice of this invention can be added from water solutions or suitable organic solvent solutions may be used. The compounds can be added during various pro-

cedures including those described in Collins et al., U.S. Pat. No. 2,912,343 issued Nov. 10, 1959; McCrossen et al., U.S. Pat. No. 3,342,605 issued Sept. 19, 1967; Audran U.S. Pat. No. 2,996,287 issued Aug. 15, 1961 and Johnson et al., U.S. Pat. No. 3,425,835 issued Feb. 4, 1969.

The photographic layers used in the practice of this invention 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 issued June 15, 1954. If desired, two or more layers may be coated simultaneously by the procedures described in Russell U.S. Pat. No. 2,761,791 issued Sept. 4, 1956; Hughes U.S. Pat. No. 3,508,947 issued Apr. 28, 1970; and Wynn British Pat. No. 837,095 issued June 9, 1960. This invention also can be used for silver halide layers coated by vacuum evaporation as described in British Pat. No. 968,453 issued Sept. 2, 1964 and LuValle et al. U.S. Pat. No. 3,219,451 issued Nov. 23, 1965.

The photographic and other hardenable layers used in the practice of this invention can be hardened by various organic or inorganic hardeners, alone or in combination, such as the aldehydes, and blocked aldehydes as described in Allen et al. U.S. Pat. No. 3,232,764 issued Feb. 1, 1966; ketones, carboxylic and carbonic acid derivatives, sulfonate esters, sulfonyl halides and vinyl sulfonyl ethers as described in Burness et al U.S. Pat. No. 3,539,644 issued Nov. 10, 1970; active halogen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodiimides, polymeric hardeners such as oxidized polysaccharides like dialdehyde starch and oxyguargum and the like.

The following examples further illustrate the invention.

EXAMPLE 1

In order to determine the amount of lateral diffusion of dye or dye spread in a diffusion transfer system, the following elements are prepared:

A. Mordant Coating

An opaque cellulose acetate support is coated with a coacervate mordant dispersion of the type described in U.S. Pat. No. 3,271,147 of Bush, issued Sept. 6, 1966, at a coverage of 163 mg/ft^2, and then a gelatin overcoat at a coverage of 640 mg/ft^2.

B. Emulsion Coating

A cellulose acetate support is coated with a gelatin-silver bromide emulsion (150 mg silver/ft^2 and 500 mg gelatin/ft^2), coupler solvent diethyl lauramide (101 mg/ft^2), and cyan dye-forming image transfer coupler

1-hydroxy-4[α-(3'-pentadecylphenoxy)butyramido]-phenoxy-N-ethyl-(2'', 5''-dicarboxy)-2-naphthanilide (101 mg/ft^2).

The following developing solution is prepared:

4-amino-N-ethyl-N-β-hydroxyethylaniline — 11 g
ascorbic acid — 0.385 g
Sodium carbonate — 22 g
Potassium bromide — 0.825 g
Sodium sulfite — 2 g
Water to — 1.1 liter

Samples of the Emulsion Coating are then given a 10, 100 and 1000 micron x-ray line exposure. Samples of the Mordant Coating, the Emulsion coating and a Nuclepore membrane, 0.5 micron pore size, 10 microns thick, open area about 8 percent, pore density 4.2×10^7/cm^2, are then dipped for five seconds in the developing solution described above.

One of the Mordant Coatings is laminated directly to a sample of the Emulsion Coating while the other laminated sample has the Nuclepore membrane in-between. After two minutes, the samples are separated and then washed. A microdensitometric trace of the transferred images reveals very little difference in dye spread and only a small difference in density. Since there was no loss of sharpness, this proves that the pores are straight-through.

EXAMPLE 2

Example 1 is repeated with the addition of a second control of a gelatin interlayer having the same swollen thickness as the Nuclepore membrane. After the microdensitometric traces are obtained, measurements are made of the width of the trace both at the bottom and halfway up. The following results are obtained:

	10 μ		100 μ		1000 μ	
	b.w.*	h.w.**	b.w.*	h.w.**	b.w.*	h.w.**
No interlayer	56	25	33	17	105	83
Gelatin interlayer	92	46	40	18	110	88
Nuclepore	69	27	37	15	109	86

*Width of trace measured in units along the bottom
**Width of trace measured in units halfway up

It is seen that the gelatin interlayer produces considerable spreading of dye density as evidenced by the largest width of the trace, especially at the 10μ exposure, while the Nuclepore interlayer almost maintains the sharpness of the control.

EXAMPLE 3

A sample of the Nuclepore membrane is coated with a thin layer (50 mg/ft^2) of gelatin. The swollen thickness of the gelatin layer is about 1–2 microns. Several such coated membranes are laminated together. The purpose of the gelatin coat is to provide a little space for dye molecules to wander to find the pores of the next layer, since it would be impossible to align holes of two adjacent membranes. Laminates containing one, two and three Nuclepore layers are then processed as in Example 1. The following red densities are obtained:

	Red D_{max}
Control	2.98
One Nuclepore Layer	2.55
Two Nuclepore Layers	2.28
Three Nuclepore Layers	2.0

While the density decreases because of the added thickness of the Nuclepore membranes, the sharpness is approximately the same as the control since the pores are straight-through.

The invention has been described with particular reference to certain 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. In a photographic element comprising a support having thereon a dye image-receiving layer, a substantially opaque light-reflective layer and at least one photosensitive silver halide emulsion layer having a dye image-providing material associated therewith capable of reacting with oxidized developing agent to produce a dye, the improvement wherein:

a. said support is a porous, polymeric material with pore diameters ranging from about 0.5 to about 12 microns and a porosity of from about 1 to about 25 percent, and

b. all of said layers not being located on the same side of said support.

2. The photographic element of claim 1 wherein said polymeric material is a hydrophilic polycarbonate.

3. The photographic element of claim 1 wherein said dye image-receiving layer and said light-reflective layer are on one side of said support and said photosensitive layer is on the other side of said support.

4. The photographic element of claim 3 wherein said polymeric material is a hydrophilic polycarbonate.

5. The photographic element of claim 1 wherein the photosensitive portion comprises red-, green- and blue-sensitized silver halide emulsion layers having cyan, magenta and yellow dye image-providing materials, respectively, associated therewith.

6. A photographic element comprising a porous, polymeric support having pore diameters ranging from about 0.5 to about 12 microns and a porosity of from about 1 to about 25 percent having on one side thereof in the order recited:

a. a substantially opaque, light-reflective layer; and

b. a dye image-receiving layer; and having on the other side thereof in the order recited:

aa. a red-sensitive silver halide emulsion layer having a dye image-providing material associated therewith capable of reacting with oxidized developing agent to produce a diffusible cyan dye;

bb. a green-sensitive silver halide emulsion layer having a dye image-providing material associated therewith capable of reacting with oxidized developing agent to produce a diffusible magenta dye; and

cc. a blue-sensitive silver halide emulsion layer having a dye image-providing material associated therewith capable of reacting with oxidized developing agent to produce a diffusible yellow dye.

7. A photographic film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members comprising:

I. a photosensitive element comprising a support having thereon a dye image-receiving layer, a substantially opaque, light-reflective layer, and at least one photosensitive silver halide emulsion layer having a dye image-providing material associated therewith capable of reacting with oxidized developing agent to produce a dye, said support being a porous, polymeric material with pore diameters ranging from about 0.5 to about 12 microns and a porosity of from about 1 to about 25 percent, all of said layers not being located on the same side of said support;

II. a transparent sheet superposed over said silver halide emulsion layer of said photosensitive element; and

III. a rupturable container containing an alkaline processing composition having therein an opacifying agent, said rupturable container being positioned transverse a leading edge of said photosensitive element so that a compressive force applied to said container by said pressure-applying members will effect a discharge of the container's contents between said transparent sheet and said underlying silver halide emulsion layer of said photosensitive element adjacent thereto.

8. The photographic film unit of claim 7 wherein said polymeric material is a hydrophilic polycarbonate.

9. The photographic film unit of claim 7 wherein said dye image-receiving layer and said light-reflective layer are on one side of said support and said photosensitive layer is on the other side of said support.

10. The photographic film unit of claim 7 wherein the photosensitive portion of said photosensitive element comprises red-, green- and blue-sensitized silver halide emulsion layers having cyan, magenta and yellow dye image-providing materials, respectively, associated therewith.

11. A photographic film unit which is adapted to be processed by passing said unit between a pair of juxtaposed pressure-applying members, comprising:

I. a photosensitive element comprising a porous, polymeric support having pore diameters ranging from about 0.5 to about 12 microns and a porosity of from about 1 to about 25 percent having on one side thereof in the order recited:

a. a substantially opaque, light-reflective layer; and

b. a dye image-receiving layer; and having on the other side thereof in the order recited:

aa. a red-sensitive silver halide emulsion layer having a dye image-providing material associated therewith capable of reacting with oxidized developing agent to produce a diffusible cyan dye;

bb. a green-sensitive silver halide emulsion layer having a dye image-providing material associated therewith capable of reacting with oxidized developing agent to produce a diffusible magenta dye; and

cc. a blue-sensitive silver halide emulsion layer having a dye image-providing material associated therewith capable of reacting with oxidized developing agent to produce a diffusible yellow dye;

II. a transparent sheet superposed over said blue-sensitive silver halide emulsion layer of said photosensitive element; and

III. a rupturable container containing an alkaline processing composition having therein an opacifying agent, said rupturable container being positioned transverse a leading edge of said photosensitive element so that a compressive force applied to said container by said pressure-applying members will effect a discharge of the container's contents between said transparent sheet and said blue-sensitive silver halide emulsion layer of said photosensitive element adjacent thereto.

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