United States Patent [19]

Young

[11] **3,881,932**

[45] **May 6, 1975**

[54] **PHOTOGRAPHIC PRODUCTS WITH STRIPPABLE OPAQUE LAYERS**

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[73] Assignee: **Polaroid Corporation,** Cambridge, Mass.

[22] Filed: **Oct. 3, 1973**

[21] Appl. No.: **403,037**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 239,582, March 20, 1972, abandoned.

[52] **U.S. Cl.** ..... **96/76 R;** 96/76 C; 96/83; 96/84 R

[51] **Int. Cl.** **G03c 1/48;** G03c 1/90; G03c 1/84

[58] **Field of Search** ..... 96/29 R, 76 R, 84 R, 83, 96/76 C, 71

[56] **References Cited**

UNITED STATES PATENTS

2,565,378	8/1951	Land	96/76 C
3,316,198	4/1967	Van Gorder et al.	96/83
3,351,470	11/1967	McCune	96/3
3,677,790	7/1972	Bishop et al.	96/84 R

FOREIGN PATENTS OR APPLICATIONS

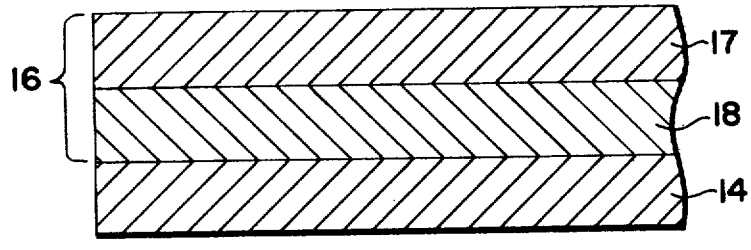
972,050	10/1964	United Kingdom	96/67

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Assistant Examiner—Richard L. Schilling
Attorney, Agent, or Firm—Philip G. Kiely

[57] **ABSTRACT**

This application is directed to diffusion transfer photographic products especially useful as film units in film packs or the like. Essentially the photographic products presented comprise a photosensitive element which after processing can provide a useable negative which is preferably produced concurrently with the formation of a positive image pattern.

17 Claims, 3 Drawing Figures



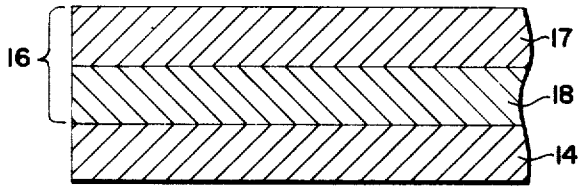


FIG. 1

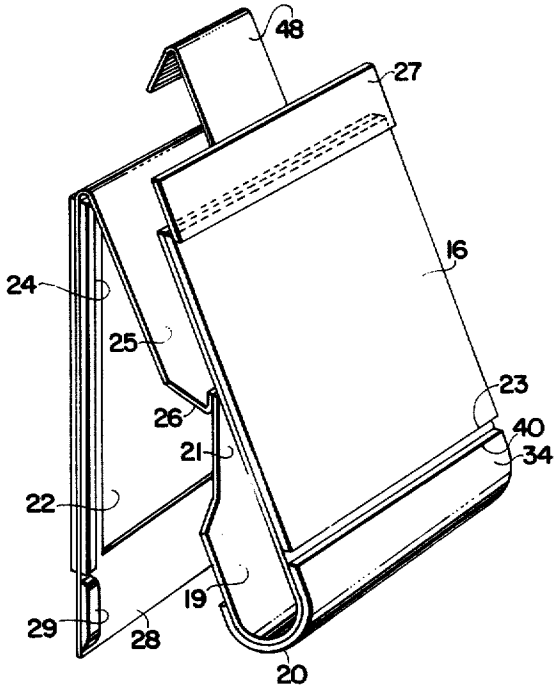


FIG. 2

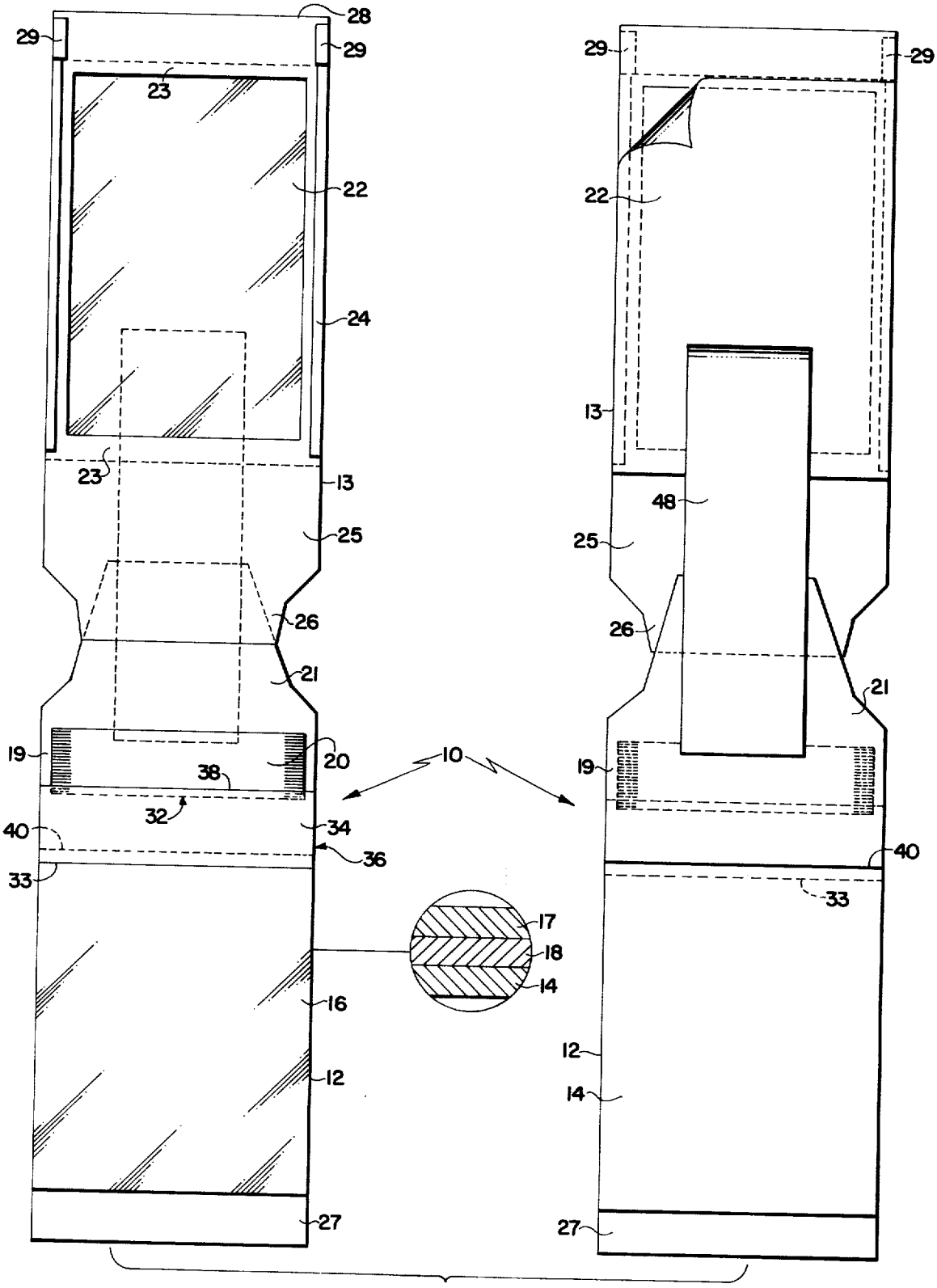

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FIG. 3

PHOTOGRAPHIC PRODUCTS WITH STRIPPABLE OPAQUE LAYERS

CROSS REFERENCE TO OTHER APPLICATIONS

This application Ser. No. 239,582, filed Mar. 20, 1972, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to diffusion transfer photography. More precisely, the invention disclosed herein relates to diffusion transfer photographic film units or products which can be developed outside of a camera after exposure and can provide a developed, usable negative concurrently with the formation of a positive transfer image pattern.

2. Description of the Prior Art

The present invention is concerned with photographic film units, particularly adapted for employment in a photographic film pack or film magazine of the type shown in U.S. Pat. No. 3,080,805, issued Mar. 12, 1963, in the name of Joel A Hamilton, comprising a container, at least one film unit mounted for exposure within the container and a closure element for preventing the admission of light into the container. As disclosed in that patent, each film unit includes, in combination, a first photosensitive element positioned for exposure within the container; a second nonphotosensitive element, preferably a print-receiving element, adapted to be superposed with the photosensitive element during withdrawal of the film unit from the container, following exposure thereof; and frangible container means particularly adapted to releasably retain a fluid processing composition for distribution between the superposed photosensitive and printreceiving elements after photoexposure of the film unit.

In general, the film pack or container includes an exposure aperture adapted to permit exposure of the photosensitive element; a removable closure element located across the exposure aperture; at least one film unit; and an opening permitting withdrawal of the closure element and film units from the container successively through this opening. The closure element and each film unit includes a leader adapted to project from the film pack through the opening whereby to provide means for selectively withdrawing the closure element, or a film unit, from the film pack into contact, and in engagement, with means adapted to provide individual distribution of the retained fluid processing composition, between superposed photosensitive and nonphotosensitive elements.

Film packs of this type are intended to be employed in photographic apparatus, such as a camera, which include means for maintaining a film pack in position for exposure, means for selectively exposing the photosensitive element of successive film units of the pack, and means for engaging each film unit during withdrawal from the pack, after photoexposure, and distributing the retained processing fluid between, and in contact with, the contiguous photosensitive and print-receiving elements of the film unit, for effecting photographic diffusion transfer processing of the respective, photoexposed film unit. Processing of each film unit may thus be effected manually by grasping a leader attached to the film unit and withdrawing the leader and film unit from both the pack and the camera.

In photographic diffusion transfer processing, the photosensitive sheet element is normally first exposed and then biased into superposed relationship with a second sheet element, which is, in general, photographically inert and aids in the controlled distribution of the processing composition. The photosensitive element may contain an integral print-receiving stratum or the second sheet element may comprise a transfer image-receiving element. The contiguous sheet elements are moved relative to, and between, a pair of suitably opposed members such as gapped parallel pressure rollers or platens. Application of pressure to the frangible fluid-retaining means effects controlled rupture thereof and predetermined unidirectional distribution of its processing composition contents between, and in contact with, the opposed surfaces of the superposed elements. After transfer processing, the image-carrying area of the printreceiving element may be separated from the laminate.

As those skilled in the art know, useable, i.e., fully developed and fixed negatives have been heretofore obtained using diffusion transfer photographic products, e.g., film units and techniques. Details relating to such products and techniques can be found, for example, in U.S. Pat. No. 2,705,676, issued to Edwin H. Land and Howard G. Rogers on Apr. 5, 1955, and in U.S. Pat. No. 3,345,166, issued to Edwin H. Land, Meroe M. Morse and Elizabeth L. Yankowski on Oct. 3, 1967. Also film products designated as Polaroid Type 55 Film (Polaroid Corporation, Cambridge, Massachusetts) are commercially available and can simultaneously provide useable negatives as well as positive image patterns. However, as those skilled in the art also know, useable negatives have not been obtained in photographic film units of the type described before, e.g., photographic film units for use in a photographic film pack or film magazine such as disclosed in the aforesaid U.S. Pat. No. 3,080,805. The present invention is particularly addressed to this long outstanding problem in the art and provides distinctive film units which can provide a developed, useable negative which is preferably formed concurrently with the formation of a positive image pattern.

SUMMARY OF THE INVENTION

The present invention is directed to photographic products comprising a photosensitive element which after processing, i.e., development and fixing, and, optionally, formation of a positive image, can provide a substantially transparent image-bearing member and which is distinctively adhered to an opaque plastomeric sheet material. Photosensitive elements of the type presented by the present invention are particularly useful for providing film units which can be developed outside a camera and the photosensitive elements are especially adaptable for use in film packs or magazines of the type described before. Essentially, the preferred products of the present invention employing the novel photosensitive elements comprise first and second sheet elements coupled together across their leading end sections. The first sheet element comprises an opaque plastomeric sheet material having an optical density of at least about 6 and preferably at least about 9. Other essential members of the first sheet element are a photosensitive element comprising a photosensitive layer coated on a pellucid, e.g., substantially transparent or translucent layer adhered to a surface of an

opaque plastomeric sheet material. The opaque plastomeric sheet material is distinctive in that it comprises an opacifying system, e.g., a pigment or dye, dispersed in a polymeric matrix which can provide an effective adherent capability between the pellucid layer and the plastomeric sheet material until the sheet material is contacted with a fluid, e.g., a liquid or gas, which can cause swelling of the polymeric material of the matrix. In other words, the polymeric material provides a tight bond to the photosensitive sheet material in the dry state only. Upon swelling, the polymeric material no longer provides an adherent capability and the plastomeric sheet material separates or can be separated from the photosensitive element.

The second sheet member has an opaque support and can function merely as a spreader sheet. Preferably, however, the second sheet member carries on one surface thereof a diffusion transfer image-receiving element so arranged and positioned that the receiving element can receive a diffusion transfer image pattern from the photosensitive element when the first and second sheet members are placed in superposition and a fluid processing composition is distributed between the photosensitive and receiving elements.

The film units of the present invention further include a rupturable container containing a processing composition. In the preferred embodiment of the present invention the rupturable container is carried on the surface of the first sheet member between the leading edge thereof and the photosensitive element. In accordance with the manners well known to the art, the contents of the container are distributed between the photosensitive and image-receiving elements to thereby affect processing as the film unit is passed between pressure applying members.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a fragmentary side view of a preferred arrangement of the essential elements of the essential members of the photosensitive elements of the present invention;

FIG. 2 is a fragmentary perspective view of a photographic film unit embodying the invention;

FIG. 3 is a front and rear plane view of the film unit of FIG. 2.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The film units of the present invention are especially adaptable for use in a film pack or magazine comprising a plurality of individual film units. Each film unit includes a photosensitive element, a second element, preferably a printreceiving element which can be superposed with the exposed photosensitive sheet during processing, and a rupturable container of processing fluid. Processing of the film unit is effected in the camera by a pair of pressure-applying members, preferably rolls, which engage the film unit as the latter is withdrawn from the camera and distribute a processing fluid from the container in a layer between the photosensitive and printreceiving elements. Each film unit includes a leader which serves as means, projecting from the camera, to be grasped for pulling the film unit from the camera between the pressureapplying members.

Reference is initially made to FIG. 1 where there is shown a fragmentary, cross-sectional view of the essential members of the photosensitive element of the present invention.

The opaque plastomeric sheet member **14** provides partial protection for the photosensitive element **16** after the unit has been removed from the camera and until processing is complete. Accordingly, sheet member **14** preferably has an optical density of at least about **6** over the entire visible spectrum and preferably has an optical density of at least about 9. Also member **14** is a thin, substantially fluid swellable plastomeric sheet material preferably having a thickness no greater than about 3 mils but having sufficient strength to resist tearing and wrinkling during the exposure, the withdrawing of the unit from the camera and the development of the film unit.

In accordance with the practice of the present invention member **14** includes an opacifying system comprising a pigment or dye dispersed in a polymeric matrix having distinctive characteristics. Specifically the polymeric material comprising the matrix is characterized in that it can provide an effective adherent capability between sheet member **14** and base member **18** until such time as member **14** is contacted with a fluid which causes the polymeric material to swell. Upon swelling, the preexisting adherent capability is diminished to the extent that member **14** can be easily removed from member **18.**

The opacifying system included in member **14** can—as mentioned—comprise a pigment or dye dispersed in the polymeric matrix to provide an optical density for the layer sufficient to prevent transmission of substantially all of the light incident thereon. The preferred pigment is carbon black but mixtures of other pigments, e.g., titanium dioxide, iron oxides etc. can also be suitably employed. Dyes can also be dispersed in the polymeric matrix of sheet member **14** to render the sheet opaque and such dyes can be used alone or in combination with pigments to obtain the desired function.

The polymeric matrix of sheet member **14** comprises a polymeric material which can be swollen but is not soluble to any significant degree in the particular fluid employed to remove sheet member **14** from base member **18** of photosensitive element **16.** As those skilled in the art know, the degree of swellability of a polymeric material as opposed to the degree of solubility of the material in the fluid employed for removal will vary depending primarily on the polymeric material(s) and/or the fluid(s) employed. However, in the practice of the present invention the balance between the swellability and solubility characteristics is such that the primary affect of the fluid on the polymeric material is to cause swelling of the material rather than dissolving the material to any significant extent so that sheet member **14** can be removed from base member **18** as one piece or in large pieces rather than as flakes or dispersed particles.

Especially suitable polymeric materials useful in the practice of the present invention includes those which can provide thin layers of high tensile and tear strength as well as the desired degree of swellability discussed above. The desired degree of swellability can be obtained by the selection of the proper combination of polymeric material and fluid. For example, many polymeric materials can be rendered swellable in a particular fluid by cross linking techniques or the like. Also many polymeric materials are known which are soluble

in a fluid at one temperature but are only swellable by the fluid at other temperatures.

In the especially preferred embodiment of the present invention a sodium sulfite solution is employed as the fluid to remove sheet member **14** from base member **18.** Accordingly, the especially preferred polymeric materials are those which are swellable but substantially insoluble in sodium sulfite solutions wherein the sodium sulfite can vary in concentration, for example, from about 0.5% by weight to about 30% by weight. Suitable specific polymeric materials include partially and fully hydrolyzed polyvinyl alcohols, polyacrylamides, carboxyalkyl celluloses and the like. The following Table illustrates specific combinations of opacifying and polymeric materials which can be coated on a polyester base member **18** to provide suitable sheet members **14** (0.8 mil thick) of the type to which the present invention pertains.

TABLE 1

(Parts by Weight)

	1	2	3	4	5	6	7	8	9	10
Carbon black	7	7	7	6	6	6	6	6	6	
Elvanol 70-05 [1]	17	—	—	12	12	12	12	—	—	—
Elvanol 51-05[2]	—	17	—	—	—	—	—	12	12	12
Lemoflex 219[3]	—	—	17	—	—	—	—	—	—	—
Glycerine	—	—	—	1.8	1.8	1.8	—	1.8	—	—
Glyoxal	—	0.8	—	—	—	—	—	1.8	—	—
Triton X-100[4]	0.5	0.5	0.5	0.4	0.4	0.4	—	0.4	0.4	0.4
Carboset 515[5]	—	—	—	—	7.2	—	—	—	—	—
Tecpol AZ-44[6]	—	—	—	—	—	1.9	1.9	—	—	—
Carbowax 200[7]	—	—	—	—	—	—	1.8	—	1.8	1.8
Ammonium dichromate	—	—	—	—	—	—	—	—	1.8	—
Boric acid	—	—	—	—	—	—	—	—	—	0.09
Water to give approximately 20% solids										

1. A fully hydrolyzed, hot water-soluble polyvinyl alcohol sold by E. I. DuPont de Nemours, Inc., Wilmington, Del.

2. A partially hydrolyzed, cold water-soluble polyvinyl alcohol sold by E. I. DuPont.

3. A chemically modified, cold water soluble polyvinyl alcohol sold by Borden Chemical Co., New York N. Y.

4. A non-ionic wetting agent sold by Rohm & Haas Corporation, Philadelphia, Pa.

5. An alkali-soluble acrylic resin sold by B. F. Goodrich, Co., Cleveland, Ohio.

6. A poly(hydroxypropyl acrylate) sold by Raffi and Swanson, Inc., Wilmington, Mass.

7. A water-soluble polyethylene glycol sold by Union Carbide Corporation, New York, N. Y.

A particularly preferred sheet member is composed of the following:

	Parts by Weight
Elvanol 70-05	3.3
Elvanol T-25[8]	10
Carbon black	6.6
GAF S-630[9]	5
Voranol RN-485[10]	2.8

8. A medium molecular weight, fully hydrolyzed polyvinyl alcohol sold by E. I. DuPont de Nemours, Inc., Wilmington, Del.

9. A polyvinylpyrrolidone/vinyl acetate copolymer sold by GAF Corp., New York, N. Y.

10. A polyether polyol sold by the Dow Chemical Company, Midland, Mich.

From the foregoing, it will be seen that in addition to the swellable polymeric material, the formulation may also contain various additives such as wetting agents, adhesion promoters, cross-linking agents and aids to release.

Substantially any fluid which will swell the polymeric material sufficiently to provide the desired loss in adhesive capability may be employed in the practice of the present invention. Since the preferred polymeric materials comprise water-swellable materials, it is preferred that water be employed as the swelling medium; more preferably, an aqueous solution of sodium sulfite. In a particularly preferred embodiment, hardeners are employed in the fluid to minimize scratching on the reuseable negative. Similarly, organic salts may also be employed to assist in maintaining the integrity of the separated polymeric material so that it will not go into solution or "crumble" in the fluid tank. Thus, a particularly preferred fluid comprises:

Glutaraldehyde bis(sodium bisulfite) addition product[11]	65 g.
Sodium citrate	125 g.
Water	to make 1 liter

11. Prepared according to the procedure of U.S. Pat. No. 3,232,761, issued Feb. 1, 1966.

Base member **18** is adhered to opaque back coat **14** and after being separated from opaque layer **14** provides a pellucid support for photosensitive layer **17.** Accordingly, layer **18** can be fabricated of any material which can obtain the desired function. Especially preferred are those synthetic or naturally occurring polymeric materials which can provide substantially transparent, flexible support members. Accordingly, layer **18** may comprise any of the various types of transparent flexible supports, for example, polymeric films of both the synthetic type and those derived from nautrally occurring products, etc. Especially suitable materials, however, comprise flexible transparent synthetic polymers such as polymethacrylic acid, methyl and ethyl esters; vinyl chloride polymers; polyvinyl acetals; polyamides such as nylon; polyesters such as the polymeric films derived from ethylene glycol terepthalic acid; polymeric cellulose derivatives such as cellulose acetate, triacetate, nitrate, propionate, butyrate, acetate-butyrate, or acetate propionate; polycarbonates; polystyrenes; and the like.

It should be understood that although transparent base member **18** is shown as one layer, more than one discrete layer of different polymeric materials can be employed to provide the assigned function of member **18.**

The photosensitive layer **17** of element **16** can comprise one or more of the silver halides, such as photosensitive silver chloride, silver iodide, silver bromide, and preferably, mixed silver halides, such as silver chlorobromide, silver iodochloride, silver iodobromide or silver iodochlorobromide, of varying halide ratios and the silver concentrations dispersed in a processing composition permeable binder material such as gelatin and the like. Mixed silver halides comprising silver iodobromide and iodochlorobromide are especially preferred, particularly those comprising about 1 to 9% iodide by weight of silver.

The preferred silver halide type photosensitive layers employed for the fabrication of the photographic film unit, may be prepared by reacting a water-soluble silver salt such as silver nitrate with at least one water soluble halide, such as ammonium, potassium or sodium chloride, preferably together with corresponding iodide and bromide, in an aqueous solution of a peptizing agent such as colloidal gelatin solution; digesting the dispersion at an elevated temperature, to provide increased crystal growth; washing the resultant dispersion to remove undesirable reaction products and residual water-soluble salts, for example, employing the preferred gelatin matrix material, by chilling the dispersion, noodling the set dispersion, and washing the noodles with cold water, or, alternatively, employing any of the various floc systems, or procedures, adapted to effect removal of undesired components, for example, the procedures described in U.S. Pat. Nos. 2,614,928; 2,614,929; 2,728,662, and the like; after ripening the dispersion at an elevated temperature in combination with the addition of gelatin or such other polymeric material as may be desired and various adjuncts, for example, chemical sensitizing agents and the like; all according to the traditional procedures of the art, as described in Neblette, C. B., Photography — Its Materials and Processes, sixth Ed., 1962.

Optical sensitization and preferably panchromatic sensitization of the emulsion's silver halide crystals may then be accomplished by contact with optical sensitizing dye or dyes; all according to the traditional procedures of the art, or described in Hamer, F. M. *The Cyanine Dyes and Related Compounds.*

After optical sensitization, any further desired additives, such as coating aids and the like, may be incorporated in the emulsion and the mixture coated according to the conventional photographic emulsion coating procedures known in the art.

As the binder for the photoresponsive material, the aforementioned gelatin may be, in whole or in part, replaced with some other natural and/or synthetic processing composition permeable polymeric material such as albumin; casein; or zein or resins such as cellulose derivative, as described in U.S. Pats. Nos. 2,322,085 and 2,541,474; vinyl polymeric such as described in an extensive multiplicity of readily available U.S. and foreign patents or the photoresponsive material may be present substantially free of interstitial binding agent as described in U.S. Pat. Nos. 2,945,771; 3,145,566; 3,142,567; Newman, *Comment on Non-Gelatin Film, B. J. O. P.*, 434, Sept. 15, 1961; and Belgian Pat. Nos. 642,557 and 642,558.

An especially preferred feature of photosensitive element **16** of the present invention involves the integration of anti-light piping capability with the element so that such elements can be processed outside the camera to provide transparencies having image patterns free from effects of any potential "light piping." Light piping is a phenomenon well known to the photographic art and usually involves light passing through the edges or ends of a film which is then scattered, reflected or otherwise transmitted to portions of the photosensitive system to cause fogging thereof. In the film units of the present invention, the potential for such fogging especially as the units are withdrawn from the camera is effectively eliminated by integrating an anti-light piping capability with the photosensitive element. The anti-light piping capability can be included in the photosensitive system, e.e., layer **17** but in the preferred embodiment the capability comprises a layer **18** having a photosensitive system **17** coated thereon and layer **18** comprises a plastomeric sheet material having dispersed therein a pigment or chemical system which can effectively prevent light piping. The pigment and chemical systems providing the effective anti-light piping capability are further characterized in that at least after processing, they do not prevent transmission of substantially all the light incident on the layer containing the system. Accordingly, after processing, layer **18** with photosensitive system **17** can be removed from plastomeric member **14** to provide image bearing transparencies.

Particulate pigments are especially suitable in the practice of the present invention and include those that may or may not strongly absorb light but those that strongly absorb are especially preferred. Representative pigments include finely divided titanium dioxide, alumina, silica, barium sulfate and carbon with carbon blacks including graphite being especially preferred.

In the especially preferred embodiment of the present invention, a finely divided particulate carbon is dispersed in a substantially transparent plastomeric sheet material, such as polyethylene terephthalate. The finely divided carbon may be a graphite, lamp black, bone black, furnace black, channel black or thermal black. The average particle diameter of such carbon blacks may, for example, range between 9 millimicrons to about 500 millimicrons, as measured with an electron microscope. Carbon blacks having an average particle diameter below about 100 millimicrons are preferred.

The amount of carbon dispersed in layer **18** can vary somewhat depending upon such factors as the species of carbon involved and the particle size thereof. However, the best balance of desired properties is obtained by dispersing an amount of carbon sufficient to provide a layer which has an optical density as measured on the side of the layer at 700 mμ—of at least about 5.0 and preferably to about 6.0, the amount being insufficient to prevent transmission of substantially all of the light incident on the surface of the layer. In a transparent layer about 4 mils thick, this amount can correspond to between about 10 to about 30 mgms. carbon per ft.^{2} The carbon can be dispersed in the transparent layer such as by milling together the carbon and polymeric material comprising the layer and sheeting out the dispersion in the form of a film of the desired thickness.

Quite surprisingly, transparent layers comprising a dispersion of the above described minor amount of carbon effectively prevent fogging of the photosensitive layer after the unit has been removed from the camera. Equally important, the minor amount dispersed in the layer does not adversely diminish the transparency of the combination of layer **18** and **17** but for all practical purposes, the combination of layers remains effectively transparent and high quality reproductions of the image pattern obtained in layer **17** can be prepared therefrom.

In accordance with the practice of the present invention, other pigments which can absorb, diffuse or otherwise prevent transmission of radiation that can fog portions of the photosensitive layer until processing is complete can be employed in layer **18** either alone or in combination with carbon. The effective amount of such pigments can vary depending upon the particular pigment and other considerations related, for example, to the effect of the pigment on exposure time and on ultimate image quality. For example, a substantially transparent layer having 1% by weight titanium dioxide dispersed therein can be employed in the practice of the present invention.

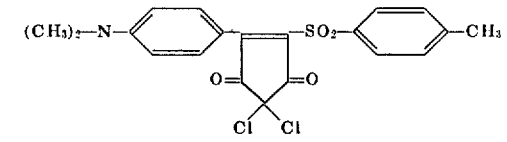
Also as mentioned, chemical systems can also be dispersed in plastomeric materials to provide layer **18** having an anti-light piping capability. Such chemical systems include a reagent or reagents having the capability of rendering the layer light absorbing before exposure, but also having the capability of interacting with the processing fluid employed to reduce the light absorbing characteristics of the layer, e.g., a reagent or reagents providing the requisite absorptive protection at a first pH but which are substantially transparent at a second pH supplied by the processing fluid. Also the reagent or reagents are those that can interact with diffusion transfer image processing composition to be "discharged" so that layers containing the products of the interaction are rendered effectively transparent, and hence do not interfere with viewing of the negative image pattern.

Particular reagents especially suitable in the practice of the present invention are dyes known to the art as "antihalation dyes." Such dyes can be readily dispersed in a plastomeric matrix to provide sheets or layers initially having the light absorption capability of the aforementioned characteristics. Alternatively, dispersions of such dyes can be coated on other layers of the photographic product to provide suitable auxiliary protective layers. In addition to providing layers that are initially light absorbing, the antihalation dyes can interact with diffusion transfer image processing compositions so that the diffusion transfer image pattern can be viewed in or through layers containing the products of the interaction.

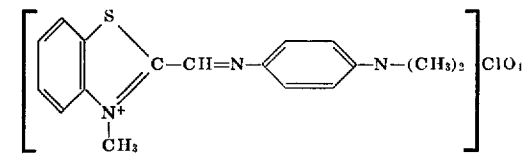
As mentioned, antihalation dyes are known to the art. They are described, for example, in U.S. Pat. Nos. 3,471,293; 3,469,985; 3,440,051; 3,389,994; 3,384,487; 3,364,029; 3,352,680; 3,340,062; and 3,005,711 and in British Pat. No. 515,998, all of which are incorporated herein by reference. Particularly preferred are those anti-halation dyes which can provide the desired absorption capability initially, but which interact with the processing composition at a rapid rate so that the absorption capability initially present is cleared quickly from the dye-containing layer. Triarylmethane dyes, for example, are especially suitable in the present invention.

Representative dyes suitable in the practice of the present invention include the following, among others:

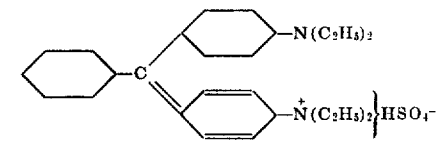
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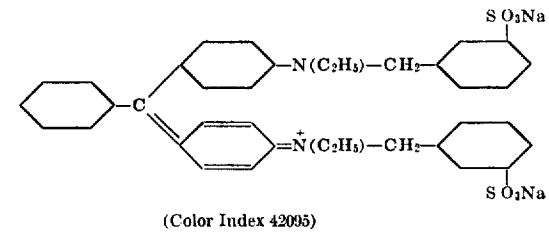


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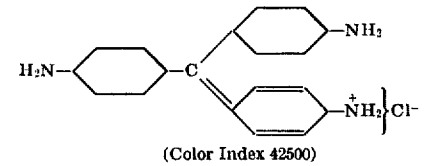
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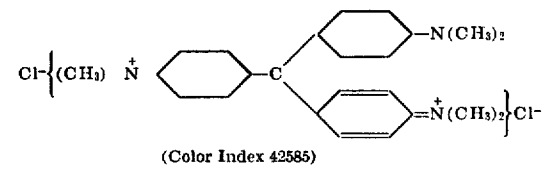
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5.



(Color Index 42500)

6. Zinc double chloride of—



(Color Index 42585)

The amount of dye or dyes required to provide an effective anti-light piping capability can vary depending upon the particular dye or combination thereof employed. However, the best balance of desired properties is obtained when the amount employed is sufficient to provide a layer which initially has an optical density—as measured on the side of the layer at 700 mμ—of at least about 5.0 and preferably 6.0. In most instances, the amount of dye required to provide the desired optical density is extremely low with respect to the matrix material of the film containing the dye. For example, with certain dyes or combinations thereof suitable protective films can be obtained by employing 2 milligrams of dye per 5 grams of polymer.

Reference is now made to FIGS. **1** through **3** of the drawings wherein there are illustrated film units of the present invention which can be employed in photographic products of U.S. Pat. No. 3,080,805. Each film unit designated **10** comprises a first sheet element **12** and a second sheet element **13.** First sheet element **12** has as essential elements thereof photosensitive ele-

ment **16** which comprises an opaque sheet material **14** adhered to base layer **18** which, as mentioned, preferably provides an anti-light piping capability for photosensitive system **17**. Second sheet element **13** has a support which is opaque to activating radiation for photosensitive element **16** and can merely serve to aid in the distribution of a processing fluid in contact with layer **17** containing the photosensitive system. However, in the preferred film units, second sheet element **13** comprises a diffusion transfer image receiving stratum arranged on element **13** so that said stratum can receive a diffusion transfer image pattern when elements **12** and **13** are in superposition.

First sheet element **12** has a leading end **19** which is approximately equal in width to photosensitive element **16** and provides means for mounting a rupturable container **20** containing processing fluid. Leading end section **19** is securely adhered to surface **17** of element **16** between trailing edge **33** of end section **19** and leading edge **62** of element **16** and sheet material **14** and also includes a tapered end section **21**. First sheet element **12** further includes a trailing end section **27** preferably attached to the surface of photosensitive layer **17** of element **16** in the manner shown in detail in the front and rear views of FIG. **3**.

Second sheet element **13** functions as a carrier sheet for image receiving element **22** which is approximately equivalent in width to second sheet element **13**. Element **13** further has a rectangular opening **23** which provides a border about image receiving element **14** which border defines the area of receiving element **22** in which image formation can occur. Side guards **24** are secured to the side edges of second sheet element **13** providing the boundary about opening **23** to provide means to facilitate retention of the processing fluid between photosensitive element **16** and image receiving element **22** when these elements are in superposition.

Second sheet element **13** also includes a leading edge portion **25** having a tapered end portion **26** similar to tapered end portion **21**. The tapered end sections, e.g., **21** and **26**, are secured together to define the leading end section of the film unit **10** to be advanced between pressure applying members.

The length of sheet elements **12** and **13** is substantially equal and by virture of this arrangement, the sheets are readily superposed in registered relation during the processing of the film unit. Trailing end section **27** of sheet element **12** extends beyond the trailing edge of photosensitive element **16** to coact with trailing end section **28** of sheet **13** to trap any excess processing fluid which may be carried beyond the trailing ends of the photosensitive element **16** during distribution of the processing fluid. Distribution of the processing fluid, as noted, is effected by advancing sheet elements **12** and **13** and container **20** of precessing fluid, while elements **12** and **13** are in superposition between pressure-applying members. The pressure-applying members, e.g., opposed rolls, apply compressive pressure to the sheets progressively, beginning in the area of the container, to eject the fluid contents of the container between and in contact with the opposed surfaces of the photosensitive element **16** and receiving element **22**. To aid in trapping of excess fluid, spacing members **29** may be provided on trailing end section **28** adjacent the margins thereof for spacing apart the pressure-applying members to provide a gap between trailing end section **27** and trailing end section **28** in which any excess processing fluid may be collected and retained.

Upon superpositioning of elements **16** and receiving element **22**, the integrity of the so formed laminate may be maintained during processing by mechanical means such as, for example, a plurality of polymeric hooks, e.g., nylon hooks, appropriately positioned on one contact surface and a plurality of filamentary loops on the second contact surface, such as the closure materials sold by Velcor Corporation, Manchester, N. H. Also, a continuous or discontinuous adhesive layer or layers can be employed to form a seal between elements **16** and **22** to thereby facilitate processing external the camera in the presence of activating radiation. Such adhesive means may comprise a commercial pressure-sensitive adhesive such as that sold by the National Cash Register Co., Dayton, Ohio, under the trade designation P01B-101 as a pressure activated capsular adhesive, and the like, so employed that the elements may be readily separated upon completion of processing by application of minimal force to the respective components.

The rupturable container can be of the type shown and described in U.S. Pat. Nos. 2,543,181; 2,634,886; 2,653,732; 2,674,532; 2,702,146; 2,723,051; 2,750,075; 3,056,491; and 3,056,492, and can comprise a rectangular blank of fluid- and air-impervious sheet material folded longitudinally upon itself to form two walls which are sealed to one another along the longitudinal and end margins to form a cavity in which the processing fluid is contained. Longitudinal marginal seal **32** is made weaker than the end seal so as to become unsealed in response to hydraulic pressure generated within the fluid contents of the container by the application of compressive pressure to the walls of the container. Container **20** is mounted on opaque sheet **12** with the longitudinal marginal seal directed toward the trailing edge **33** of end section **19**. Bib sheet **34** is secured to opaque sheet **12** and at edge **38** on container **20**, and facilitates restricted unidirectional flow of fluid contents of container **20** after rupture thereof. Edge **40** of bib sheet **34** terminates short of trailing edge **33** of end section **19** so that the flow of fluid contents from container **20** is directed to and distributed over layer **17** of element **16**.

For details concerning the composition of the processing fluid, reference may be had to aforementioned U.S. Pat. Nos. 2,705,676 and 3,345,166.

As was mentioned, film units of the present invention are particularly useful as assemblage units of photographic film packs. The manners and methods for integrating the present film units in such film packs as well as the apparatus and structural elements involved are all set forth in the aforesaid U.S. Pat. No. 3,080,805 which is expressly incorporated herein by reference. Essentially a plurality of such film units are included in the pack which is designed to be accommodated within a camera so that the photosensitive surface **17** of first sheet member **12** of each film unit can be exposed to an image pattern of activating radiation. After exposure, the film unit is withdrawn from the exposure station and film pack in a fashion so that photosensitive layer **17** and image receiving layer **22** are in a superposed relationship and the processing composition of container **20** can be distributed between these layers.

Tab **40** provides convenient means for withdrawing each unit from the pack.

After removal of the film unit from the camera and formation of a silver transfer image, a high quality usable negative is obtained by separating opaque sheet **14** and photosensitive element **16** from leading end section **19** of element **12** such as by tearing sheet **14** with element **16** from end section **19.** After separation from end section **19,** sheet **14** and element **16** are contacted with a fluid which can cause the polymeric matrix of sheet **14** to swell so that sheet **14** can be removed as from base member **18.** In the preferred embodiment of the present invention sheet **14** is removed as a single piece and removal is complete within about a minute or less. Since sheet **14** is not soluble to any appreciable extent in the removal fluid employed the sheet can be removed from the fluid without contamination of the fluid by the matrix material of sheet **14.** This feature is important when the removal fluid also contains other ingredients which can fix or harden or otherwise treat the emulsion surface of member **16.**

A positive diffusion transfer image pattern containing element can be obtained by separating receiving element **22** from second sheet member **13** in the manner shown in the rear view of FIG. **3.**

As can be appreciated from the foregoing detailed description, the essence of the invention resides in the novel photosensitive elements presented which comprise an opaque plastomeric sheet material releasably adhered to a photosensitive system preferably integrated with a distinctive anti-light piping capability which can provide—after processing and removal from the opaque plastomeric sheet material—a substantially transparent image-bearing member useful in providing high quality reproductions. Accordingly, the novel photosensitive elements are especially useful in diffusion transfer photographic products particularly those described in the above detailed description of the preferred embodiment. However, since certain changes can be made in the above disclosed products without departing from the spirit and scope of the essence of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photosensitive element which comprises a photosensitive silver halide layer coated on a pellucid plastomeric layer and an opaque plastomeric sheet material having an optical density of at least about 6.0 adhered to said plastomeric layer on the said opposite said silver halide layer, said sheet material comprising a substantially water-insoluble fluid swellable polymeric material adapted to lose adhesive capability upon swelling, thereby separating from said pellucid layer.

2. A photosensitive element of claim **1** which includes a pigment or chemical system which can (1) provide an effective anti-light piping capability for said photosensitive element and (2) which at least after processing of said photosensitive system after exposure thereof can provide a layer which can transmit substantially all of the light incident on the surface of said layer; and an opaque plastomeric sheet material having an optical density of at least about 6.0 strippably adhered to said plastomeric layer.

3. A photosensitive element of claim **1** wherein said photosensitive silver halide layer is coated on a plastomeric layer comprising an antihalation dye which can initially provide an effective anti-light piping capability for said photosensitive element but which can interreact with a processing fluid applied to said photosensitive element after exposure thereof to provide a layer which can transmit substantially all of the light incident on the surface of said layer.

4. A photosensitive element of claim **1** wherein said photosensitive silver halide is coated on a plastomeric layer comprising a pigment in an amount sufficient to provide an effective anti-light piping capability for said photosensitive element but insufficient to prevent transmission of substantially all of the light incident on said layer.

5. A photosensitive element of claim **1** wherein said opaque plastomeric sheet material comprises a polymeric material chosen from the group consisting of polyvinyl alcohol, polyacrylamides, carboxyalkycelluloses and mixtures of these.

6. A photosensitive element of claim **5** wherein said opaque plastomeric sheet material comprises a carbon black as the opacifying material.

7. A photosensitive element of claim **1** wherein said photosensitive system is coated on a plastomeric layer having a carbon black dispersed therein in an amount sufficient to provide an optical density for said layer as measured on a side thereof of at least about **5.0.**

8. A photosensitive element which comprises a photosensitive silver halide system coated on a substantially transparent plastomeric layer having a carbon black dispersed therein in an amount sufficient to provide an optical density for said layer as measured on a side thereof at least about 5.0 and an opaque plastomeric sheet coated on the side of said transparent plastomeric sheet opposite said photosensitive silver halide system, said sheet having an optical density of at least about 6.0, said sheet material comprising a substantially water-insoluble fluid swellable polymeric material adapted to lose adhesive capability upon swelling, thereby separating from said transparent plastomeric layer.

9. A photographic product which can be developed outside a camera after exposure of the product and adapted to provide a substantially transparent image bearing element after said product is processed by passage between pressure applying members, said product comprising first and second opaque sheet elements coupled across their leading end sections, said first member comprising in order, a silver halide photosensitive layer coated on a pellucid plastomeric layer and an opaque plastomeric sheet material having an optical density of at least about 6.0 adhered to said pellucid plastomeric layer said sheet material comprising a substantially water-insoluble, fluid swellable polymeric material adapted to lose adhesive capabiltiy upon swelling, thereby separating from said pellucid layer; said second sheet element comprising an opaque sheet adapted to be superposed said first sheet element after exposure of said photosensitive layer as said product is withdrawn from a camera and a rupturable container retaining processing composition arranged in relation with said first and second elements to distribute processing composition between said photosensitive system and said superposed element as said product is passed between pressure-applying members.

10. A product of claim **9** which includes a pigment or chemical system which can (1) provide an effective an-

ti-light piping capability for said photosensitive layer and (2) which at least after processing of said photosensitive layer after exposure thereof can provide a layer which can transmit substantially all of the light incident on the surface of said layer.

11. A photographic product of claim **9** wherein said second element further includes an image receiving stratum which can receive a diffusion transfer image pattern from said photosensitive layer when said elements are brought into superposition.

12. A photographic product of claim **11** wherein said pellucid plastomeric layer comprising an antihalation dye which can initially provide an effective anti-light piping capability for said photosensitive layer but which can interreact with said processing fluid applied to said photosensitive layer after exposure thereof to provide a layer which can transmit substantially all of the light incident on the surface of said layer.

13. A photographic product of claim **11** wherein said photosensitive layer includes a pigment in an amount sufficient to provide an effective anti-light piping capability for said photosensitive layer but insufficient to prevent transmission of substantially all of the light incident on said layer.

14. A photographic product of claim **11** wherein said pellucid plastomeric layer includes a carbon black dispersed therein in an amount sufficient to provide an optical density for said layer as measured on a side thereof of at least about 5.0.

15. A photographic product of claim **11** wherein said opaque plastomeric sheet material is selected from the group consisting of polyvinyl alcohol, polyacrylamides, carboxyalkyl celluloses and mixtures of these.

16. A photographic product of claim **11** wherein said opaque plastomeric sheet material comprises a carbon black as the opacifying material.

17. A photographic product of claim **10** which comprises a photosensitive silver halide system coated on a substantially transparent plastomeric layer having a carbon black dispersed therein in an amount sufficient to provide an optical density for said layer as measured on a side thereof of at least about 5.0 and an opaque plastomeric sheet having an optical density of at least about 6.0 adhered to said layer, said sheet material comprising a polyvinyl alcohol.

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