

March 15, 1966

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3,240,604

PHOTOGRAPHIC PRODUCTS CONTAINING POLYTETRAFLUOROETHYLENE LAYER

Filed Feb. 18, 1963

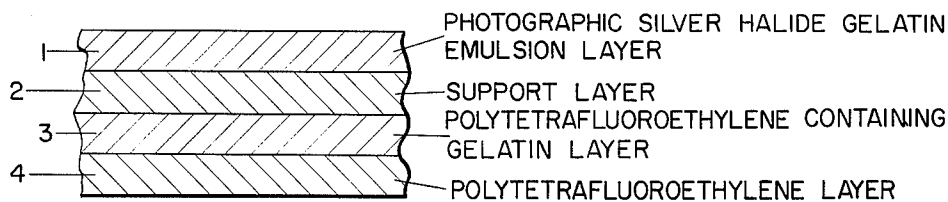


FIG. 1

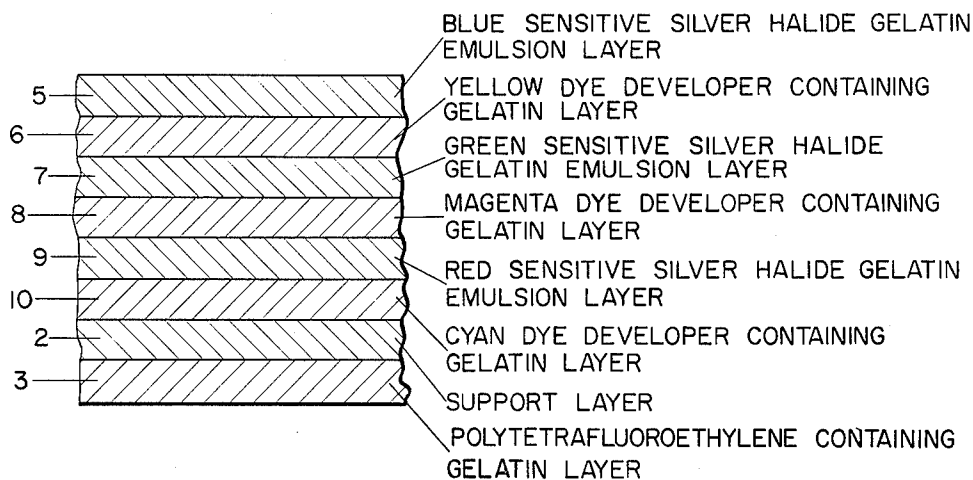


FIG. 2

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PHOTOGRAPHIC PRODUCTS CONTAINING
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Filed Feb. 18, 1963, Ser. No. 259,084

1 Claim. (Cl. 96—73)

This invention relates to photographic elements and, more particularly, to composite photographic elements which comprise a plurality of layers, including a support layer, a silver halide gelatin emulsion layer on one side of said support layer, and a polytetrafluoroethylene containing layer located as an external layer of said plurality of layers.

Under conditions of general commercial employment, composite photographic film elements are stored as packaged film rolls or film packs for periods of months prior to their actual use. During such storage, the sheet material is under varying parameters of compressive pressures and, in addition, may be subjected to a wide variety of environmental stresses or extremes, as, for example, varying temperature conditions and relative humidities.

In that the film rolls and film packs must maintain a high degree of efficiency and reliability during storage, the component sheet materials must be prevented from interactions which would affect their structural integrity or dimensional stability, whereby their ultimate photographic employment would be impaired.

In particular, photographic film elements which comprise a support or film base having one or more gelatin layers coated on one or both sides of the support must be prevented from adhering or blocking when stacked, for example, gelatin layer contacting gelatin or other polymeric layer, in a film pack, or when a gelatin layer containing sheet film is rolled upon itself, as occurs in roll film.

In the past, such adhesion or blocking has been prevented, in general, by the addition of relatively large amounts of conventional gelatin hardening agents, as, for example, inorganic agents providing polyvalent metallic atoms, especially polyvalent aluminum or chromium ions, for example, potash alum [$K_2Al_2(SO_4)_4 \cdot 24H_2O$] and chrome alum [$K_2Cr_2(SO_4)_4 \cdot 24H_2O$], and organic agents of the aldehyde type such as formaldehyde, glyoxal, mucochloric acid, etc., the ketone type such as diacetyl, the quinone type, etc., to a gelatin layer positioned such as to be subject to blocking.

The use of the last-mentioned relatively large amounts of such hardening agents gives rise to a serious problem of controlling the disposition of such agents, so as to insure that they do not migrate from the layer in which they are deposited and deleteriously contaminate a photosensitive silver halide gelatin layer of the film unit.

Objects of the present invention are therefore to provide photographic films which include at least one gelatin containing layer and are particularly adapted to alleviate blocking during storage of same.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the product possessing the features, properties and the relation of components which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For the fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawing wherein:

FIGURE 1 is a diagrammatic fragmentary cross-sectional view of a photographic film product of the present invention particularly adapted for employment in monochromatic photographic processes; and

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FIG. 2 is a diagrammatic fragmentary cross-sectional view, similar to FIGURE 1, and illustrates a photographic element of the present invention particularly adapted for employment in multichromatic photographic processes.

It has now been found that blocking, which is especially serious when film units, stored as previously noted, attain temperatures above 85° F. and relative humidities above 80%, may be prevented by locating a layer comprising polytetrafluoroethylene as an external layer of the film unit.

The polytetrafluoroethylene containing layer may be located as the distal layer on either or both sides of the support and may additionally contain one or more polymeric film-forming components such as gelatin, one or more modifying agents such as hardening agents, plasticizers, etc., for such components, and one or more coating aids to facilitate fabrication of the layer.

Preferably the polytetrafluoroethylene containing layer is located on the support on the side opposite the photosensitive strata and may be there deposited by conventional coating techniques adapted to distribute a coating solution comprising a dispersion of discrete polytetrafluoroethylene granules, preferably of colloidal size and dispersed in a polymeric film-forming solution.

For purposes of simplicity, an aqueous coating solution is preferred although it will be readily recognized that an organic coating system, for example, a system employing one or more liquid hydrocarbons as the solvent, or a coating system utilizing a coating solution containing dispersed aqueous and organic phases, may also be employed where desired.

In a preferred embodiment, the concentration of polytetrafluoroethylene present falls within the range of about 0.05 to 10 parts polytetrafluoroethylene per part of polymeric film-forming resin, by weight.

The polymeric film-forming component of the preferred coating solution may be a synthetically derived thermoplastic polymer such as poly-4-vinyl pyridine which may be coated from an acetic acid-water system, cellulose nitrate which may be coated from an ethyl acetate system, cellulose acetate butyrate which may also be coated from an ethyl acetate system, a mixture of such polymers, for example, poly-4-vinyl pyridine in acetic acid and water in combination with cellulose nitrate in ethyl acetate, etc., or one of the naturally occurring film-forming polymers such as gelatin, casein, etc.

Where desired, one or more conventional coating aids such as saponin, etc., and/or conventional polymeric modifiers, for example, plasticizers such as glycerine, glycols, sorbitol, etc., hardeners such as those previously enumerated, etc., may be included in the coating composition to facilitate the selected coating process employed and to provide desired properties to the resultant polymeric film. It will be recognized that the specific choice of addenda is extremely broad and will be determined, in part, by the polymeric resin employed, the conditions of coating, and the physical and chemical properties desired of the resultant film.

FIGURE 1 of the accompanying drawing illustrates a composite photographic element which comprises a support layer 2, a photographic silver halide gelatin emulsion layer 1 located on one surface of support layer 2, a polytetrafluoroethylene containing gelatin layer 3 located on the opposite surface of support layer 2, and a polytetrafluoroethylene layer 4 located on the surface of layer 3 located distal to support layer 2.

A multilayer subtractive multicolor film unit particularly adapted for use in the photographic processes of

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U.S. Patent No. 2,983,606, issued May 9, 1961, and the copending U.S. application of Edwin H. Land and Howard G. Rogers, Serial No. 565,135, filed February 13, 1956, is illustrated in FIG. 2, of the accompanying drawing. The illustrated photosensitive element comprises: a support layer 2, a gelatin layer 10 containing cyan dye developer, a red-sensitive silver halide gelatin emulsion layer 9, a gelatin layer 8 containing magenta dye developer, a green-sensitive silver halide gelatin emulsion layer 7, a gelatin layer 6 containing yellow dye developer, and a blue-sensitive silver halide gelatin emulsion layer 5, mounted on one surface of support layer 2, and a gelatin layer 3 containing polytetrafluoroethylene and, preferably, additionally containing a gelatin hardening agent, mounted on the opposite surface of support layer 2.

The invention will be illustrated in greater detail in conjunction with the following specific examples which set out representative utilization of the novel concepts of this invention, which, however, are not limited to the details therein set forth and are intended to be illustrative only.

EXAMPLE 1

1.33 mls. of an aqueous polytetrafluoroethylene dispersion (sold by E. I. du Pont de Nemours & Co., Wilmington, Delaware, under the trade designation Teflon T-30 and comprising an aqueous dispersion containing approximately 60% polytetrafluoroethylene, by weight), was added to 80 mls. of a 10% gelatin solution, at 65° C. To this mixture was added 10 mls. of an aqueous 3% solution of oxidized starch sold by Miles Chemical Company, Clifton, New Jersey, under the trade designation Sumstar 190.

The final mixture contained 8.9% gelatin, 0.89% polytetrafluoroethylene and 0.33% oxidized starch, by weight, and was coated immediately on the cellulose acetate film base surface of a multicolor photographic film of the type described in explanation of FIG. 2.

In general, the photosensitive film unit comprised a cellulose acetate film base or support carrying a red-sensitive silver halide gelatin emulsion stratum, a green-sensitive silver halide gelatin emulsion stratum and a blue-sensitive silver halide gelatin emulsion stratum; said emulsions having dispersed in water-immiscible organic solvents and contained in separate alkali-permeable gelatin layers behind the emulsion strata, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. The particular dye developers employed in the photosensitive elements were 1,4-bis-(α -methyl- β -hydroquinonyl-ethylamino)-5,8-dihydroxyanthraquinone (a cyan dye developer); 2-(p-[2',5'-dihydroxyphenethyl]-phenylazo)-4-isopropoxy-1-naphthol (a magenta dye developer); and 1-phenyl-3-n-hexyl-carboxamido-4-(p-[hydroquinonylethyl]-phenylazo)-4-pyrazolone (a yellow dye developer). The last-mentioned yellow and magenta dye developers are disclosed in the copending U.S. application of Blout et al., Serial No. 145,978, filed October 18, 1961 and the cyan dye developer is disclosed in the copending U.S. application of Blout et al., Serial No. 233,461, filed October 26, 1962, now U.S. Patent No. 3,135,606.

A film unit prepared as set forth above, and a control film unit prepared as set forth above except that the polytetrafluoroethylene component was omitted, were stored in roll form at 100° F. and 90% relative humidity for 16 hours.

The control roll blocked so severely as to be incapable of being unrolled without substantial destruction of the film unit's structural integrity and photographic utility while the polytetrafluoroethylene containing film unit exhibited no blocking and no impairment of its photographic utility.

As examples of additional formulations, for employment in the general procedure of Example 1, mention may be made of:

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(A)

Aqueous dispersion of polytetrafluoroethylene (sold under the trade name Teflon TD 3 by E. I. du Pont de Nemours & Co., Wilmington, Delaware) -----cc--		5.0
Tween 20 (trade name of Atlas Powder Company, Wilmington, Delaware, for a nonionic surface-active emulsifying agent comprising complex esters of fatty acids and polyhydric materials) -----cc--		3.0
One-half sec. cellulose nitrate -----g--		16.6
Ethyl acetate -----cc--		75.4

(B)

Aqueous dispersion of polytetrafluoroethylene (TD 3) -----cc--		1.50
Poly-4-vinylpyridine -----g--		2.3
Glacial acetic acid -----cc--		2.35
Water -----cc--		93.80

(C)

One-half sec. cellulose nitrate -----g--		4.24
Ethyl acetate -----cc--		19.20
Poly-4-vinylpyridine -----g--		1.68
Glacial acetic acid -----cc--		1.68
Water -----cc--		69.10
Aqueous dispersion of polytetrafluoroethylene (TD 3) -----cc--		2.76
Tween 20 -----cc--		1.34

Photosensitive elements prepared, employing each of the aforementioned compositions, respectively, exhibit substantially no blocking and/or impairment of their photographic utility, when subjected to the test procedures of the preceding example.

EXAMPLE 2

A photosensitive film unit containing the plurality of associated photosensitive silver halide gelatin layers and dye developer containing gelatin layers detailed in Example 1 on one surface and a gelatin layer on the opposite surface of the film base, was coated with an aqueous dispersion of polytetrafluoroethylene deposited on the external surface of the last-mentioned gelatin layer in a concentration of 10-15 mgs. of solids per square foot.

The film unit was then stored in roll form at 100° F. and 90% relative humidity for 16 hours and exhibited no blocking and/or impairment of its photographic utility.

EXAMPLE 3

The procedure of Example 2 was repeated except that the aqueous polytetrafluoroethylene dispersion was coated on the external surface of the film unit's blue-sensitive silver halide gelatin emulsion layer.

EXAMPLE 4

10 mls. of Teflon T-30 was added, at 20° C., to 80 mls. of a 10% gelatin solution. To this mixture was added 4 mls. of a 5% mucochloric acid solution.

The final mixture contained 10.6% gelatin, 6.4% polytetrafluoroethylene, and 0.21% mucochloric acid, by weight, and was coated on the cellulose acetate film base of a multicolor photographic film unit of the type described in Example 1, at a thickness of 17 microns.

3.5 mls. of Teflon T-30 was then mixed with 80 mls. of a 2.5% gelatin solution, at 65° C.

The mixture contained 2.4% gelatin and 2.5% polytetrafluoroethylene, by weight, and was coated as the external layer of the plurality of associated photosensitive emulsion and dye containing gelatin layers, at a thickness of 5 microns.

Subjection of the film units of Examples 3 and 4 to the test procedure of Example 2 provided substantially identical results. Furthermore, no loss of acuity, speed, or dye transfer is observed when the film units are employed in the diffusion transfer photographic processes of the

aforementioned U.S. Patent No. 2,983,606 and application Serial No. 565,135.

It will be recognized that the polymeric layers formulated in accordance with the instant disclosure, e.g., the polytetrafluoroethylene containing gelatin layers of the examples, may additionally contain various addenda such as, for example, silver halide developing agents.

Employment of film units, prepared in accordance with the aforementioned examples, in photographic film packs, for example, of the type disclosed in U.S. Patent No. 3,002,437, issued October 3, 1961, and subjecting them to the environmental conditions previously described provides results analogous to those described with reference to roll film testing.

In general, such film packs comprise an envelope or magazine containing a plurality of photographic elements or films adapted to be withdrawn therefrom, singularly, and in a predetermined sequence. As disclosed in the last-stated U.S. patent, such photographic elements may comprise an assemblage including a first photosensitive sheet element adapted to be exposed and placed in superposed relationship with a second sheet element adapted to receive a photographic diffusion transfer image and processed by a suitable processing composition included in the assemblage.

It has quite unexpectedly been found that a gelatin layer containing polytetrafluoroethylene absorbs considerably less water, for example, in the order of one-half or less the normal amount of absorbed water, depending upon the concentration of polytetrafluoroethylene, than is absorbed by such layer in the absence of the polytetrafluoroethylene, when stored at 90% relative humidity and 100° F. for approximately 48 hours. This increase in the water resistancy characteristics of a gelatin layer containing polytetrafluoroethylene may be postulated to

be the result of a hardening action for which no logical explanation yet appears.

Since certain changes may be made in the above product without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

- 10 A photographic product which comprises a plurality of layers including a support layer, located on one surface of said support layer a cyan dye developer-containing gelatin layer, a red-sensitive silver halide gelatin emulsion layer, a magenta dye developer-containing gelatin layer, 15 a green-sensitive silver halide gelatin emulsion layer, a yellow dye developer-containing gelatin layer, and a blue-sensitive silver halide gelatin emulsion layer, and located on the opposite surface of said support layer a gelatin layer containing discrete polytetrafluoroethylene granules present in a concentration within the range of 20 0.05 to 10 parts polytetrafluoroethylene per part of gelatin.

References Cited by the Examiner

UNITED STATES PATENTS

25	2,322,037	6/1943	Lindquist	96—94
	2,495,111	1/1950	Land	96—76 X
	2,876,131	3/1959	Kumnick et al.	260—92.1
	3,077,400	2/1963	Rogers et al.	96—73 X
30	3,146,102	8/1964	Weyerts et al.	96—3

FOREIGN PATENTS

718,232 11/1954 Great Britain.

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