

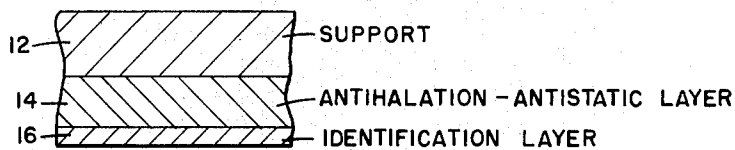
Dec. 7, 1965

G. F. NADEAU ETAL

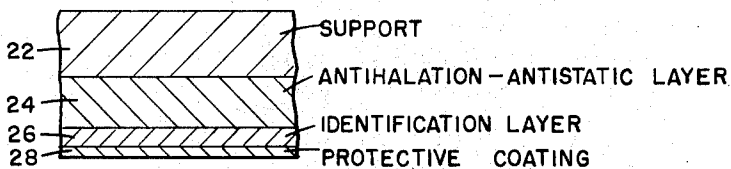
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COMPOSITE FILM ELEMENT

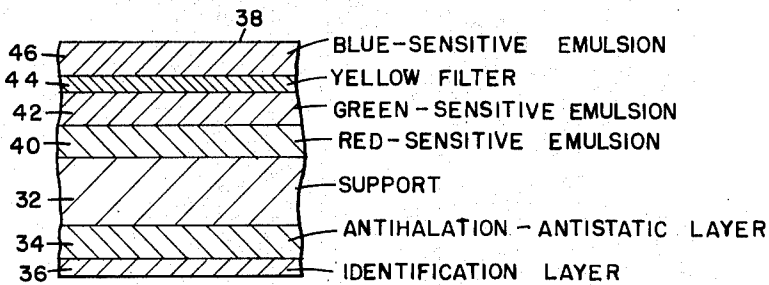
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10 **Fig. 1**



20 **Fig. 2**



30 **Fig. 3**

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3,222,178

COMPOSITE FILM ELEMENT

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This invention relates to the photographic art. In particular, this invention relates to a composite film element for use in preparing photographic film products that can be easily and readily identified under conditions of extremely low level of light, and to photographic film products prepared therefrom.

Multi-layer photographic color film products have been available commercially for a number of years. In the usual sensitivity arrangement of three-layer photographic color film, a red-sensitive emulsion layer is coated adjacent a film support and this is followed in order by a green-sensitive emulsion layer and a blue-sensitive emulsion layer.

On the side of the film support opposite the applied emulsion layers there is usually applied a layer having both antihalation properties and antistatic properties. A layer that has proved to be highly satisfactory for this purpose is comprised of a water-insoluble, alkali-soluble resinous composition and carbon black in finely divided form. The carbon black is substantially uniformly distributed throughout the resinous composition.

Recently, there has been made available commercially a new and improved photographic color film product. This new and improved photographic color film product is comprised of a film support and a plurality of color-sensitive emulsion layers. This improved film product is also comprised of an antistatic and antihalation layer comprised of finely divided carbon black and a water-insoluble, alkali-soluble resin. This layer, which possesses both antistatic and antihalation properties, is applied to the surface of the film support opposite the color-sensitive emulsion layers.

These new and improved photographic color film products, after exposure, must be subjected to substantially different developing solutions and processing conditions than those employed heretofore in processing color film products. If these new color film products are not processed in the proper processing solutions, the photographic image will be destroyed.

It will be apparent therefore, that it is extremely desirable to provide a means for distinguishing these new and improved photographic color film products, when the exposed film products are being readied for processing under conditions of extremely low light level.

An object of this invention is the preparation of photographic film products which, after exposure, can be easily and readily identified by the processor under conditions of low light level so that the processor can employ the correct processing techniques in developing the exposed film product.

Another object of this invention is the preparation of a composite film element for use in preparing photographic film products that can be easily and readily identified under conditions of extremely low light level.

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

For a complete understanding of the nature and the objects of this invention, reference is made to the following detailed description and drawing, in which:

FIG. 1 is a view in cross-section of a composite film element of this invention;

FIG. 2 is a view in cross-section of a modification of the composite film element of this invention; and

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FIG. 3 is a view in cross-section of a photographic film product prepared from the composite film element of this invention.

In accordance with this invention there is provided a photographic film product comprised of a plurality of color-sensitive layers, a film support member, a specific layer having both antihalation and antistatic properties, and a specific identification layer.

Further, in accordance with this invention, there is provided a composite film element for use in preparing photographic color film products comprised of a film support member, a specific layer having both antihalation and antistatic properties, and an identification layer of specific composition bonded to the layer having antistatic and antihalation properties.

The film support member employed in this invention can be any of the well-known conventional film support members that have been employed heretofore in the photographic art. Examples of suitable film support members include those prepared from cellulose derivatives such, for example, as cellulose nitrate, cellulose acetate, and other lower fatty acid esters of cellulose including simple and mixed esters, such as cellulose propionate, cellulose butyrate, cellulose acetate propionate, cellulose acetate butyrate, and the like. Film support members prepared from ethers of cellulose, such as the ethyl ether, benzyl ether, and the like can be employed. Other suitable film support members include polyvinyl acetal film, film prepared from the superpolyamides, and film prepared from polyesters such as polyethylene terephthalate.

The antihalation-antistatic layer that is applied to a surface of the film support member to prepare the composite film element of this invention is comprised of a water-insoluble, alkali-soluble resin and finely divided carbon black. The carbon black is substantially uniformly dispersed throughout the resin.

The alkali solubility of the resin is preferred so that it can be easily and readily removed from the film support when subjected to treatment in an alkaline photographic processing solution.

Suitable water-insoluble, alkali-soluble resins for use in preparing the antihalation-antistatic layer are well known in the photographic art and include copolymers of alkyl methacrylates and methacrylic acid, carboxy resinic lactones, polyvinyl phthalate, polyvinyl acetate phthalate, and ethyl cellulose phthalate. Other suitable resins include the cellulose organic acid esters containing dicarboxylic acid groups such as cellulose acetate phthalate, cellulose acetate maleate, cellulose acetate succinate, cellulose acetate propionate phthalate, cellulose acetate propionate maleate, and cellulose acetate propionate succinate.

The copolymers of alkyl methacrylates and methacrylic acid are preferably those comprised of from about 30% to 60% by weight of methacrylic acid and from 70% to 40% by weight of an alkyl methacrylate such, for example, as methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, butyl methacrylate, t-butyl methacrylate, and mixtures thereof.

The carboxy resinic lactones that are suitable for use in this invention are those disclosed in patent 2,861,056 and in application Serial No. 772,725, filed November 10, 1958, now Patent No. 3,007,901. These esters are a carboxy ester of a monohydroxycarboxylic acid of the formula $C_nH_{2n-x+1}(OH)(COOH)_x$ wherein n is an integer in the range of 1 to 5 inclusive and x is an integer in the range of 1 to 2 inclusive, and a lactone of an interpolymers of vinyl alcohol and an unsaturated α,β -dicarboxylic acid compound from the group consisting of maleic acid, fumaric acid, itaconic acid, and their an-

hydrides, the carboxy group of the carboxy ester being the carboxy group of said monohydroxycarboxylic acid. These esters are prepared by heating to at least about 60° C., in the presence of a mineral acid such, for example, as sulfuric acid, one molar proportion of an interpolymer of a vinyl organic acid ester and an unsaturated α,β -dicarboxylic acid compound from the group consisting of maleic acid, fumaric acid, itaconic acid, and their anhydrides, with at least two molar proportions of a monohydroxy acid of the formula above set forth such, for example, as malic acid, lactic acid, hydroxy butyric acid, hydroxy valeric acid, and hydroxy caproic acid. These esters can be modified further in accordance with the teachings of application Serial No. 772,725, filed November 10, 1958, above referred to. Thus, for example, a monohydric alcohol such as methanol, ethanol, propanol, butanol, or mixtures thereof can be incorporated into the reaction mixture whereby mixed ester-lactones are obtained.

Reference is hereby made to Patent 2,861,056 and application Serial No. 772,725, filed November 10, 1958, for a detailed description of the resinous carboxyester-lactones and their method of preparation.

The cellulose organic acid esters containing dicarboxylic acid groups are well known. Such resins and their method of preparation are described in Patent 2,093,462.

Polyvinyl phthalate and polyvinyl acetate phthalate resins are well known in the art. These resins and their method of manufacture are described in Patent 2,484,415, reference to which is hereby made. Thus, polyvinyl acetate phthalate can be prepared by reacting polyvinyl acetate having free and esterifiable hydroxyl groups with phthalic anhydride and pyridine, the pyridine being present in an amount less than sufficient to combine with all the carboxyl groups present after the esterification is completed. Polyvinyl phthalate is prepared in a similar manner except that polyvinyl alcohol is used as a reactant in place of the polyvinyl acetate.

The ethyl cellulose phthalates are also well-known resinous materials. The ethyl cellulose phthalates that are particularly useful in this invention have an ethoxyl content of from about 36% to 38% and a phthalyl content of from about 6% to 35%. The alkali or ammonium salts of these resins are soluble in water or in ethanol at a temperature of from about 50° F. to 70° F. These resins can be derived by the reaction of ethyl cellulose and phthalic anhydride by the method disclosed in Patent 2,753,339. Reference is hereby made to this patent.

The antihalation-antistatic layer can be prepared and applied to the film support member by any convenient method. The method disclosed and described in Patent 2,327,828 has proved highly satisfactory for this purpose. Thus, for example, the antihalation-antistatic layer or backing for the film support member can be prepared by mixing carbon black with a water-insoluble alkali-soluble resinous material such, for example, as one of the above-enumerated resins and subjecting the mixture to vigorous shearing forces while it is in the condition of a highly viscous, plastic mass so that a dispersion of the carbon black in the resinous material is formed which can be diluted with organic liquids without precipitating the carbon black from the dispersion. The dispersion is subsequently diluted with a suitable organic material such as those organic materials enumerated in Patent 2,327,828, above-referred to. Specific examples of suitable organic liquids include methyl Cellosolve, acetone, ethanol, methanol, and mixtures of two or more.

The diluted dispersion is subsequently applied to a surface of the film support member in any of the usual methods such as by immersion, by roller application, or by capillary bead application and the organic liquid evaporated therefrom. While the method of preparing a

colloidal carbon antihalation-antistatic layer as described in Patent 2,327,828, is highly satisfactory and is preferred for the purpose of this invention, other methods known in the art can be satisfactorily employed. The amount of carbon black employed in such layers can be varied over a relatively wide range, but will usually be from about .25 to .67 part by weight based on the weight of the water-insoluble, alkali-soluble resin employed.

The identification layer that is applied over the antihalation-antistatic layer is comprised of a water-insoluble, alkali-soluble resin and a pigment in finely divided form, the pigment being substantially uniformly dispersed throughout the resin.

The water-insoluble, alkali-soluble resin employed in the identification layer can be any of those set forth hereinabove as useful in forming the antihalation-antistatic layer. The preferred resin for use in preparing the identification layer is a copolymer of butyl methacrylate and methacrylic acid.

The pigment employed in the identification layer is one that will provide a layer than can be easily and readily distinguished from a black layer under conditions of extremely low light level.

Thus, in preparing photographic color film products comprised of a film support, an antihalation-antistatic layer comprising carbon black and a water-insoluble, alkali-soluble resin, and a plurality of color-sensitive emulsion layers, it is possible to leave uncoated, the antihalation-antistatic layer. The color of this layer is black owing to the presence therein of carbon black. The processor, when preparing an exposed film of this type for processing, can observe this black color and process the exposed film in the solutions designated therefor.

Those photographic color film products requiring different processing solutions will have applied over the black antihalation-antistatic layer an identification layer in accordance with this invention that is easily and readily distinguishable under conditions of low light level from the black layer. Thus, the processor can determine with ease and accuracy that such an exposed film will be required to be processed in solutions specifically designated therefor.

While various pigments can be used to provide a layer that is readily distinguishable from a black layer under conditions of low light level it is preferred to employ titanium dioxide in finely divided form in preparing the identification layer for use in this invention. An identification layer comprising titanium dioxide and a water-insoluble, alkali-soluble resin when applied over the black antihalation-antistatic layer will give a gray color. It has been determined that this gray color can be easily and readily distinguished from the black antihalation-antistatic layer under conditions of extremely low light level.

Other suitable pigments that can be employed in preparing the identification layer of this invention and that will provide a layer of a color that is readily distinguishable from black include calcium carbonate, barium sulfate, and certain silicates such as calcium silicate.

In preparing the composition comprising the pigment and water-insoluble, alkali-soluble resin for subsequent application to the black antihalation-antistatic layer, the two ingredients are admixed with a suitable organic solvent for the resin to provide a coating composition. Suitable organic solvents are well known and include acetone, methanol, ethanol, propanol, isopropanol, methyl ethyl ketone and mixtures of two or more. Usually the amount of solvent employed will be from about 24 to 48 parts by weight based on the weight of the resin. The amount of pigment employed will usually be from about .2 part to 1.0 part by weight based on the weight of the resin employed. The above proportions are given by way of example and are not critical,

and can be departed from if desired. It is well within the skill of those versed in the art to determine the proper proportions of ingredients to employ.

After application of the above composition to the black antihalation-antistatic layer, the applied coating is subjected to heat to remove therefrom substantially all the organic solvent. The thus applied identification layer is well bonded to the antihalation-antistatic layer.

A lubricant such as castor wax or the like can be subsequently applied to the applied identification layer if desired to provide thereon a protective lubricant layer. Suitable lubricants and compositions for this purpose are well known in the art. Other suitable lubricants include carnauba wax, bees wax, and certain of the petroleum waxes employed heretofore as lubricant layers.

Also it is possible to incorporate the lubricant into the identification layer if desired. If this is done the amount of lubricant employed in the identification layer will be from about .04 to .4 part by weight based on the weight of the water-insoluble, alkali-soluble resin.

The examples set forth below are illustrative of coating compositions for use in carrying out this invention. The compositions are thoroughly admixed so as to substantially uniformly disperse the titanium dioxide therein prior to application. This can be accomplished in any convenient and conventional manner such as by mixing with a power driven stirrer or by mixing in a high speed blender.

Example I

Ingredient:	Percent by weight
Resin (60% butyl methacrylate-40% methacrylic acid copolymer) -----	2.0
Titanium dioxide -----	1.5
Acetone (solvent) -----	15.0
Methanol (solvent) -----	81.5

Example II

Ingredient:	Percent by weight
Resin (60% butyl methacrylate-40% methacrylic acid copolymer) -----	2.0
Castor wax (lubricant) -----	0.1
Titanium dioxide -----	1.5
Acetone (solvent) -----	10.0
Methanol (solvent) -----	81.4
Propylene chloride (solvent) -----	5.0

Example III

Several film elements comprising a cellulose acetate film support and a black antihalation-antistatic layer are prepared. The black antihalation-antistatic layer, which is applied to one surface of cellulose acetate film support, is comprised of cellulose acetate phthalate and finely divided carbon black. The finely divided carbon black is substantially uniformly dispersed throughout the resin and is present in an amount of about .4 part by weight based on the weight of the resin.

Example IV

The composition of Example I is applied by roller application over the black antihalation-antistatic layer of one of the film elements of Example III and subsequently dried to remove therefrom substantially all the solvent. The applied layer gives a product that has a gray color and is easily and readily distinguishable, under conditions of extremely low light level, from an uncoated composite film element of Example III. Both the antihalation-antistatic layer and the applied identification layer are easily and readily removed in alkaline prebath solutions leaving the surface of the cellulose acetate film support free of foreign materials.

Example V

The composition of Example II is applied over the black antihalation-antistatic layer of one of the film elements of Example III in a manner similar to that of Example IV. Substantially the same results are obtained as set forth in Example IV.

The identification layer of this invention has no untoward effects on the antihalation and antistatic properties of the black antihalation-antistatic layer over which it is applied. Usually the thickness of the applied identification layer will be from about 25% to 75% of the thickness of the antihalation-antistatic layer. The thickness of the antihalation-antistatic layer is usually of the order of from about .00016 mil to .00024 mil.

Referring now to FIG. 1 of the drawing there is shown a composite film element 10 prepared in accordance with this invention. The composite film element 10 is comprised of a film support 12, a layer 14 having both antihalation and antistatic properties and being comprised of carbon black and a water-insoluble, alkali-soluble resin, and an identification layer 16 comprised of a pigment and a water-insoluble, alkali-soluble resin. The identification layer 16 can also have incorporated therein a small amount of a lubricant such as castor wax.

FIG. 2 of the drawing shows a modification of the invention. Shown is a composite film element 20 comprised of a film support 22, a layer 24 having antihalation and antistatic properties and being comprised of a resin and carbon black, an identification layer 26 in accordance with this invention, and a protective layer or coating 28 comprised of a lubricant such as castor wax.

In FIG. 3 of the drawing there is shown a photographic color film product 30 which is comprised of the composite film element of this invention. The film product 30 is comprised of a film support 32 carrying an antihalation-antistatic layer 34, and an identification layer 36. On the other side of the support 32 there is a color section or component 38. The color component 38 as shown is made up of a plurality of layers 40, 42, 44 and 46. As shown, layer 40 is comprised of a red-sensitive emulsion, layer 42 is comprised of a green-sensitive emulsion, layer 46 is comprised of a blue-sensitive emulsion. The exact make up of the color section 38 is not a limitation on this invention. It is sufficient to point out that the color section or component will be comprised of silver halide emulsion layers separately sensitive to the red, green, and blue spectral regions, usually in the order named, with the red-sensitive emulsion layer being adjacent the film support. The color section can also be comprised of various filter layers and the like.

It will be apparent to those skilled in the art that, by following the teachings of this invention, it is possible to provide photographic film products that can be easily and readily distinguished one from another under conditions of low light level. This ease of distinguishing one film product from another is particularly valuable and important when the film to be processed must be subjected to processing solutions and conditions entirely different from those employed in processing certain other film products.

It is to be understood that the above drawing, description and examples are illustrative of the invention and not in limitation thereof.

We claim:

1. A composite film element comprising (1) a film support, (2) a layer having antihalation and antistatic properties disposed on one surface of the film support and being comprised of finely divided carbon black and a water-insoluble, alkali-soluble resin and (3) an identification layer disposed over layer (2) comprised of finely divided titanium dioxide, a copolymer of butyl methacrylate and methacrylic acid, and castor wax.

2. A composite film element comprising (1) a film support, (2) a layer having antihalation and antistatic properties disposed on one surface of the film support, said layer being comprised of finely divided carbon black and a water-insoluble, alkali-soluble resin, (3) an identification layer disposed over said layer (2) comprised of finely divided titanium dioxide and a water-insoluble, alkali-soluble resin, and a protective lubricant layer, said lubricant layer being disposed on the identification layer (3).

3. A photographic film product comprising (1) a film support, (2) a layer having antihalation and antistatic properties disposed on one surface of the film support, said layer being comprised of finely divided carbon black and a water-insoluble, alkali-soluble resin, and (3) an identification layer disposed over said layer (2) comprised of finely divided titanium dioxide and a water-insoluble, alkali-soluble resin, (4) a plurality of silver halide emulsion layer separately sensitive to the red, green, and blue spectral regions disposed on the other side of the film support, and a protective lubricant layer, said lubricant layer being disposed over identification layer (3).

4. A photographic film product comprising (1) a film support, (2) a layer having antihalation and antistatic properties disposed on one surface of the film support and being comprised of finely divided carbon black and a water-insoluble, alkali-soluble resin, and (3) an identification layer disposed over layer (2) comprised of finely divided titanium dioxide, a copolymer of butyl methacrylate and methacrylic acid, and castor wax, and (4) a plurality of silver halide emulsion layers separately sensitive to the red, green, and blue spectral regions disposed on the other side of the film support.

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NORMAN G. TORCHIN, *Primary Examiner.*