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PHOTOGRAPHIC FILM ELEMENTS

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1

This invention relates to photographic film elements having improved anti-static properties and to a method of making the same. More particularly it relates to photographic films having at least one colloid light-sensitive silver halide layer disposed on one surface of the hydrophobic film base and a layer of a Werner type chromium-carboxylic acid complex directly imposed on the other surface. Still more particularly it relates to photographic films having a vinylidene chloride copolymer layer and a colloid silver halide emulsion layer disposed on one surface of a hydrophobic polyethylene terephthalate film base and a layer containing a Werner type chromium-carboxylic acid complex in a water-permeable binding agent directly imposed on the reverse side of the base and to a method of making the same.

In the manufacture of photographic film the phenomenon known as "static" is troublesome. This phenomenon is due to the formation and discharge of positive or negative charges during the drying, slitting, perforating, winding, packaging and other finishing operations. The discharge exposes the light-sensitive silver halides leaving characteristic marks after development. Various methods and apparatus have been proposed to eliminate the formation of static during the above operations, but they are not entirely satisfactory.

An object of this invention is to provide a simple and effective method of eliminating or minimizing "static" in the manufacture of photographic film. Another object is to provide such a method which can be practiced with the conventional types of coating equipment. A further object is to provide light-sensitive photographic film elements which have improved anti-static properties. A still further object is to provide such films from available economical materials. Still other objects will be apparent from the following description of the invention.

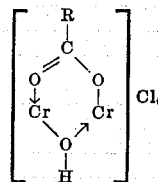
It has been found that the above objects can be attained by applying a coating composition comprising a solvent, a film-forming polymer of high molecular weight, and a Werner type chromium complex in which trivalent chromium is coordinated with a monocarboxylic acid group taken from the class consisting of saturated aliphatic carboxylic acid groups having less than 6 carbon atoms free from or bearing at least one dipole group, aromatic carboxylic acid groups having less than 8 carbon atoms and free from or containing at least one dipole group and benzoacetic acid groups having at least one dipole

2

group, to the reverse surface of a hydrophobic film base, for example, a cellulose derivative base, e. g., cellulose nitrate, cellulose acetate, cellulose propionate, cellulose acetate butyrate, etc., a synthetic resin base or a superpolymer film base, e. g., nylon, polystyrene, polyvinylchloride and polyethylene terephthalate, or such a film base having an anchoring polymer layer and/or a colloid substratum layer on the obverse surface drying the layer containing said complex and applying a colloid sublayer, a colloid silver halide emulsion layer or a plurality of such layers and/or filter layers or protective layers to the obverse surface of the film base. In cases where a plurality of layers are applied on the obverse side of the film base, the coatings are, of course, dried between each application and after the last layer has been applied. The resulting film element is then passed to a suitable windup station or cutting and packaging mechanism. During the application of the light-sensitive emulsion layer and in subsequent operations actinic light should be excluded.

The coating applied to the reverse surface of the film base that contains the Werner type chromium complex eliminates or, at least in most cases, minimizes the formation of static charges and static marks during the passage of the film through the coating apparatus where the light-sensitive colloid silver halide layer or layers and other layers are applied and during subsequent slitting, perforating, finishing, winding, packaging, etc., operations.

Werner type chromium-carboxylic acid complexes suitable for use in accordance with the invention can be represented by the general formula:



where R is an aliphatic hydrocarbon radical of less than 6 carbon atoms or such a radical containing at least one dipole group, an aralkyl radical of not more than 8 carbon atoms or such a radical containing at least one dipole radical, or an aryl radical of 6 carbon atoms or such a radical containing at least one dipole group. Among the dipole groups which can be present are Cl, Br, I, nitro, hydroxy, phenoxy, etc.

The suitable Werner type chromium-carboxylic acid complexes have been described in various chemical journals and patents. They can be made by reacting chromyl chloride with a carboxylic acid containing the radical R set forth above in a non-reactive organic solvent or diluent, e. g., carbon tetrachloride in the substantial absence of free water after the manner described in the following U. S. Patents: Iler 2,273,040, Iler 2,356,161 and Iler 2,524,803.

Among the acids which can be reacted with the chromyl chloride to form Werner complexes suitable for use in the anti-static coatings of this invention are acetic acid, propionic acid, butyric acid, valeric acid, mono-, di- and tri-chloro-bromo- and iodo-acetic acids, nitroacetic acid, hydroxyacetic acid, cyanoacetic acid; benzoic, nitrobenzoic, hydroxybenzoic, and cyano-benzoic acids; 3,5-dinitrosalicylic acid, phenylacetic acid, nitrophenylacetic acid and phenoxyacetic acid. The useful acids which contain a dipole group have moments within the range from 0.1 to 15 Debye units.

The Werner complexes are admixed with a suitable hard film-forming polymer and a suitable solvent which does not affect the complex and the resulting solution is applied to the film base by any conventional coating methods by which anti-halation or emulsion layers, etc., are applied, e. g., from extrusion orifices or transfer rollers, by skim coating, etc.

When the film-forming binding agent is a water-permeable colloid such as gelatin, albumin, agar agar; polyvinyl alcohol, hydrophilic polyvinyl esters containing a large number of $-\text{CH}_2-\text{CH}_2\text{OH}-$ groups, e. g., substantially hydrolyzed polyvinyl acetate or polyvinyl chloracetate, or hydrophilic polyvinyl acetals, containing a large number of free hydroxyl groups and acetal linkages, e. g., formal, acetaldehyde, acetal, butyral linkages, polyvinyl alcohol- and substantially hydrolyzed polyvinyl acetate-boric acid complexes; hydrophilic cellulose derivatives, e. g., ethyl cellulose, methyl cellulose, benzyl cellulose, cellulose glycolate, the colloids may be dissolved in water, water diluted with a small amount of methanol or ethanol, or methanol or ethanol.

When resinous or hydrophobic binding agents are used, e. g., vinylidene chloride/acrylonitrile copolymers, vinylidene chloride/methyl acrylate copolymers, polystyrene, vinylchloride/vinyl acetate; cellulose acetate, cellulose nitrate, cellulose propionate, etc., the binding agent is dissolved in a suitable volatile organic solvent, e. g., methyl isopropyl ketone, methyl isobutyl ketone, dioxane, cyclohexanone, benzene, acetone, methylene chloride, trichlorethane, etc., and mixtures of such solvents. The Werner complex is mixed with the solvent solution of either type binder prior to coating.

The thickness of the anti-static layer is variable from that just sufficient to form a uniform, coherent coating to a maximum thickness determined by the physical characteristics of the layer. Thus too thick a coating may lead to tackiness or flaking. While the optimum coating weight may vary depending on the binding agent and coating conditions a practical range is from about 0.2 mg. to 0.5 mg. total solids per square decimeter. The preferred coating weight for most coatings is about 0.3 mg. per square decimeter. Effective anti-static layers can be made by varying the amount of chromium complex from 0.10% to 0.30% and the amount of film-forming polymeric binder from 0.038% to 0.115% by weight of the

solvent. The Werner chromium complex should be present in an amount by weight at least twice that of the binder. The latter should be present in an amount at least sufficient to form a uniform coherent film.

After the solution of the chromium complex has been added to the film base the layer is dried for 1 to 5 minutes at a temperature from 140° to 190° F.

In the accompanying drawing which forms a part of this specification:

Fig. 1 is a schematic view of an apparatus for measuring the maximum charge buildup of a film,

Fig. 2 is a graph of test voltage values, and

Fig. 3 is a cross section of the film element of Example I.

Referring now to Fig. 1 this apparatus is a modified version of the similar apparatus described by H. W. Cleveland, *Journal of Motion Picture and Television Engineers*, vol. 55, pp. 37-44 (1950). The film, denoted as X in the figure, travels in the direction of the arrow over brass rollers A, H, G, F, E, D, C, B, all of which are thoroughly insulated from ground. F is the drive roll connected to a synchronous motor of constant speed, C is a tension roller and G is the test roller. As the film passes over roller G, there is an interchange of electrons between the surface of the film and the surface of the roller. At the instant when the film is drawn away from the roller there is found to be either an excess or deficiency of electrons on the surface of the film, leaving it with either a negative or positive charge. Thus, since this electronic process depends on the character of the materials of which the test roller and the film are made, it is possible to determine the effect that varying the composition of roller G has on the magnitude and sign of the charge built up on the film moving over the roller.

P and Q are modulators whose purpose it is to convert the electric field created by the charge on the film into a voltage which may be amplified and read on the voltmeter M₁ and M₂. A description of the modulator, which is of the rotating sector type, may be found in U. S. P. 2,494,054. Any existing charge that may be carried by the film is capable of being removed by the static eliminator T. This device ionizes the air surrounding that portion of the film which is in its immediate surroundings and allows the charge to be neutralized by attraction of ions of opposite sign to that existing on the surface of the film. A direct current voltage of varying magnitude and sign may be applied to film by the point source S.

The testing procedure is as follows: A strip of film whose dimensions are 35 mm. in width and approximately 12 feet in length is strung up as a continuous loop over the rollers A, B, C, D, E, F, G, H, as shown in Fig. 1. The motor is started to set the film into motion and the ionizer is turned on in order to remove any charge that may be present on the section of film between the ionizer and the point source S. This part of the film directly over the point source should be devoid of charge at this time. The high voltage source may now be put into operation and adjusted to provide a voltage of arbitrary magnitude and sign at the point S which in turn sprays the moving film with this same amount of voltage. This voltage is measured by the meter M₁ which has previously been calibrated. The charged film on passing over the test roller G will either acquire or accept electrons from the roller during contact and the result of this dynamic

electron transfer process is such as to cause the magnitude of charge which the film originally carried to be varied. This "leaving" charge may be measured on meter M₂. The process may be repeated, each time spraying a different amount of voltage on to the film at S. Both positive and negative values of voltage are included.

The data collected in the foregoing manner consists of sets of values of initial voltage as measured by M₁ and the corresponding leaving voltage as measured by M₂. To treat these data the voltage values are plotted on coordinate axes, the initial voltage values, M₁, being plotted on the abscissa and the leaving voltage values, M₂, being plotted as ordinates, the result being a straight line. If a line having an angle of forty-five degrees with the coordinate axes be drawn through the origin, it is seen that any point on this line has the condition that M₁=M₂, or that the initial and final values of voltage are equal. Actual results give plots whose slopes differ from unity and these lines will cross the forty-five degree line at some point such as A of Figure 2. The values of M₁ and M₂ which correspond to A are equal and the physical condition associated with this is that the electronic transfer process occurring between film and roller has attained a state of equilibrium where the number of electrons being acquired by the film is equal to the number being returned to the roller, or vice versa. This condition signifies that the value of M₁ corresponding to A or to the cross over of the plot with the forty-five degree line, will denote the maximum voltage that the film may acquire on continuous passage over rollers made of the test material. The lower that this value becomes, or similarly, the nearer the cross-point, A, approaches the origin where M₁=M₂=0, the less susceptible the film surface should be towards the accumulation of static charge.

Untreated polyethylene terephthalate film will build up a charge of about -20 kilovolts on passing over the brass rollers in the above apparatus. In comparison, polyester film base that has been treated with Werner chromium complex anti-static solutions described above and in the examples shows a maximum build-up of -0.35 to -3 kilovolts or about $\frac{1}{60}$ to $\frac{1}{15}$ that of untreated film. This decrease in maximum build-up exhibited by film treated with the chrome complex anti-static agents is sufficient to markedly reduce the tendencies for the film to show static markings.

The invention will be further illustrated but is not intended to be limited by the following examples.

Example I

An oriented film base 1 as shown in Fig. 1 of the drawing having a thickness of approximately 0.003 inch composed of polyethylene terephthalate and containing a sub-stratum layer 2 of vinylidene chloride/methylacrylate/itaconic acid copolymer of the type described in Pitzel U. S. Patent 2,570,478 on one of its surfaces was coated on the opposite side, to form an antistatic layer 4 with a solution having the following composition by weight:

	Parts	Percentage
Chromium complex of p-nitrophenylacetic acid.....	0.117	0.148
Polyvinyl alcohol/boric acid complex.....	0.045	0.057
Ethanol.....	78.90	99.795

The coating was dried at 160° F. for three minutes. The surface resistivity of the treated film is 2.1×10^{12} ohms and the maximum charge build-up that the film attains on passing continuously over brass rollers and as measured by the testing procedure previously described is -1.55 kilovolts. The surface of a second control strip of the above polyethylene terephthalate film has a surface resistance of more than 10^{16} ohms and a maximum build-up of -20 kilovolts. The side of the film containing the copolymer substratum layer was overcoated with a negative light-sensitive gelatin emulsion of the bromo-iodide type of form layer 3. The second or control film free from the Werner complex coating was provided with the same light-sensitive emulsion. The first film and the control film were slit and perforated and subjected to rapid winding and unwinding from a spool after which they were placed in the following developer for seven minutes:

	Grams
N-methyl-p-aminophenol	1.0
Hydroquinone	2.0
Potassium bromide.....	0.10
Sodium sulfite.....	50.0
Borax	7.5
Water to 1.0 liter	

The two films were washed in water and then fixed in a solution having the composition:

Sodium thiosulfate.....	grams	300.0
Sodium sulfite.....	do	11.0
Acetic acid (glacial).....	mls	13.0
Potassium alum.....	grams	10.0
Water to 1.0 liter		

On examination the film showed no fog or markings due to static whereas the control film free from the layer containing the Werner complex showed numerous "static marks."

Example II

A strip of film base composed of polyethylene terephthalate and containing a substratum layer of vinylidene chloride/methylacrylate/itaconic acid copolymer on one of its surfaces as described in Example I was coated on the opposite side with a solution having the following composition by weight:

	Parts	Percentage
Chromium complex of p-nitrophenylacetic acid.....	0.157	0.199
Polyvinyl alcohol/boric acid complex.....	0.060	0.076
Ethanol.....	78.90	99.725

The coating was dried at 160° F. for three minutes. The surface resistivity of the treated film is 5.9×10^{11} ohms and the maximum charge build-up that the film may attain on passing continuously over brass rollers and as measured by the testing procedure previously described is -0.35 kilovolt. The surface of a second control strip of the above polyethylene terephthalate film has a surface resistance of more than 10^{16} ohms and a maximum build-up of -20 kilovolts. The side of the film containing the copolymer substratum layer was overcoated with a positive light-sensitive emulsion of the bromo-iodide type. The second or control film free from the Werner complex coating was provided with the same light-sensitive emulsion. The first film and the control film were slit and perforated and subjected to rapid winding and unwinding from a spool after which

they were placed in a developing bath of the following composition for three minutes:

	Grams
N-methyl-p-aminophenol	0.7
Hydroquinone	4.2
Sodium sulfite	45.0
Potassium bromide	2.0
Sodium carbonate	28.3
Citric acid	2.0
Water to 1.0 liter	

The two films were washed in water and then fixed in a solution having the same composition as that given in Example I. On examination, the first film showed no fog or other markings due to static whereas the control film free from the layer containing the Werner complex showed numerous "static marks."

Example III

A film base composed of polyethylene terephthalate and containing a substratum layer of vinylidene chloride/methylacrylate/itaconic acid copolymer on one of its surfaces as described in Example I is coated on the opposite surface with a solution having the following composition by weight:

	Parts	Percentage
Chromium complex of p-nitrobenzoic acid	0.144	0.182
Polyvinyl alcohol/boric acid complex	0.055	0.070
Ethanol	78.90	99.748

The coating is dried at 160° F. for three minutes. The surface resistivity of the treated base is 9×10^{10} ohms and the maximum charge build-up that the film may attain on running continuously over brass rollers and as measured by the testing procedure previously described is -0.72 kilovolt.

Example IV

A film base composed of polyethylene terephthalate and containing a substratum layer of vinylidene chloride/methylacrylate/itaconic acid copolymer on one of its surfaces as described in Example I is coated on the opposite surface with a solution having the following composition by weight:

	Parts	Percentage
Chromium complex of phenylacetic acid	0.144	0.182
Polyvinyl alcohol/boric acid complex	0.055	0.070
Ethanol	78.90	99.748

The coating is dried at 160° F. for three minutes. The surface resistivity of the treated film base is 3.5×10^{11} ohms and the maximum charge build-up that the film may attain on passing continuously over brass rollers and as measured by the testing procedure previously described is +0.90 kilovolt whereas the untreated surface of a polyethylene terephthalate film when similarly passed over brass rollers will build up a charge of -20 kilovolts.

Example V

A film base composed of polyethylene terephthalate and containing a substratum layer of vinylidene chloride/methylacrylate/itaconic acid copolymer on one of its surfaces as described in Example I is coated on the opposite side with

a solution having the following composition by weight:

	Parts	Percentage
Chromium complex of trichloroacetic acid	0.144	0.182
Polyvinyl alcohol/boric acid complex	0.055	0.070
Ethanol	78.90	99.748

The coating is dried at 160° F. for three minutes. The surface resistivity of the treated film is 2×10^{11} ohms and the maximum charge build-up that the films may attain on passing continuously over brass rollers and as measured by the testing procedure previously described is -2.55 kilovolts.

Example VI

A film base composed of polyethylene terephthalate and containing a substratum layer of vinylidene chloride/methylacrylate/itaconic acid copolymer on one of its surfaces as described in Example I is coated on the opposite side with a solution having the following composition by weight:

	Parts	Percentage
Chromium complex of thioglycolic acid	0.144	0.182
Polyvinyl alcohol/boric acid complex	0.055	0.070
Ethanol	78.90	99.748

The coating is dried at 160° F. for three minutes. The surface resistivity of the treated film is 2×10^{11} ohms and the maximum charge build-up that the film may attain on passing continuously over brass rollers and as measured by the testing procedure previously described is +0.70 kilovolt.

Example VII

A film base composed of polyethylene terephthalate and containing a substratum layer of vinylidene chloride/methylacrylate/itaconic acid copolymer on one of its surfaces as described in Example I is coated on the opposite side with a solution having the following composition by weight:

	Parts	Percentage
Chromium complex of p-nitrobenzoic acid	0.156	0.154
Polyvinyl alcohol (high viscosity type)	0.075	0.074
Wetting agent (Triton X-100)	1.00	0.987
Water	100.00	98.785

The coating is dried at 160° F. for three minutes. The surface resistivity of the treated film is 1×10^{12} ohms and the maximum charge build-up that the film may attain on passing continuously over brass rollers and as measured by the testing procedure previously described is -2 kilovolts. The side of the film containing the copolymer substratum is overcoated with a positive light-sensitive emulsion of the bromo-iodide type. The film is subjected to rapid winding and unwinding from a spool after which it was processed in a similar manner to that set forth in Example II. There was no evidence of fog or other markings due to static, whereas, a similar control film having no coating on the reverse surface showed numerous static markings after development and fixing.

Example VIII

A film base composed of polyethylene terephthalate and containing a substratum layer of vinylidene chloride/methylacrylate/itaconic acid

copolymer on one of its surfaces as described in Example I is coated on the opposite side with a solution having the following composition by weight:

	Parts	Percentage
Chromium complex of p-nitrobenzoic acid	0.181	0.178
Gelatin	0.063	0.062
Wetting agent (Triton X-100)	1.00	0.988
Water	100.00	98.772

The coating is dried at 160° F. for three minutes. The surface resistivity of the treated film is 9×10^{11} ohms and the maximum charge build-up that the film may attain on passing continuously over brass rollers and as measured by the testing procedure previously described is -1.5 kilovolts.

The boric acid treated polyvinyl alcohol of the foregoing examples actually contained a small proportion of acetate groups. It contained a plurality of intralinear $-\text{CH}_2-\text{CHOH}-$ groups and some crosslinked molecules occurred in the mixture and was made as follows: a slurry of 1300 grams of 86 to 89% hydrolyzed polyvinyl acetate (having a viscosity of 4 to 6 centipoises in the form of a 4% aqueous solution) was made in 10,775 grams of 95% ethanol. The temperature was brought to 100° F., and 975 grams of boric acid added while agitating the mixture. Agitation was continued for a period of two hours during which time a polyvinyl alcohol boric acid complex was formed. Layers coated from the complex were water-insoluble but water-permeable. The preparation of polyvinyl alcohol materials of this type are described in *Irany U. S. Patent 2,326,539*.

The invention as stated above is not limited to the use of a polyvinyl alcohol boric acid complex as the binding agent for the Werner chromium complex with the above acid compounds. There may be substituted various other hydrophilic colloids as stated above. A practical one is gelatin. The vinylidene chloride/itaconic acid acrylonitrile or alkyl acrylate, etc., copolymers of *Pitzel U. S. 2,570,478* are especially useful for this purpose. The resulting layers are hydrophobic in character.

The novel anti-static layers of this invention can be applied to photographic films in general including motion picture film, multilayer color film, portrait film, lithographic film and film for recording documents, etc.

An advantage of the invention resides in the fact that it provides photographic film elements which have excellent anti-static properties. Further advantage is that the Werner type complexes are relatively inexpensive and can be applied by the conventional types of coating apparatus possessed by photographic film manufacturers. Additional advantages are that the Werner type chromium complexes are photographically inert and do not tend to fog or desensitize emulsion layers and they do not produce undesirable rough or greasy surfaces on the photographic films treated therewith.

As many widely different embodiments of this invention can be made without departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited except as defined by the claims.

What is claimed is:

1. A photographic film comprising a hydrophobic film base having on one surface a layer comprising Werner type chromium-carboxylic acid complex and a film-forming binding agent

and having disposed on the other surface at least one colloid silver halide emulsion layer, said carboxylic acid being taken from the class consisting of aliphatic carboxylic acids of less than 6 carbon atoms, aromatic carboxylic acids of 7 carbon atoms and aralkyl acids of not more than 8 carbon atoms and such acids that contain at least one dipole group.

2. A photographic film comprising a hydrophobic film base having on one surface a layer comprising Werner type chromium-carboxylic acid complex and a water-permeable binding agent and having disposed on the other surface at least one colloid silver halide emulsion layer, said carboxylic acid being taken from the class consisting of aliphatic carboxylic acids of less than 6 carbon atoms, aromatic carboxylic acids of 7 carbon atoms and aralkyl acids of not more than 8 carbon atoms and such acids that contain at least one dipole group.

3. A photographic film comprising a hydrophobic film base having on one surface a layer comprising Werner type chromium-carboxylic acid complex and a hydrophobic film-forming binding agent and having disposed on the other surface at least one colloid silver halide emulsion layer, said carboxylic acid being taken from the class consisting of aliphatic carboxylic acids of less than 6 carbon atoms, aromatic carboxylic acids of 7 carbon atoms and aralkyl acids of not more than 8 carbon atoms and such acids that contain at least one dipole group.

4. A photographic film comprising a polyethylene terephthalate film base having on one surface a layer comprising a Werner type chromium-carboxylic acid complex and a film-forming binding agent and on the other a thin layer of a vinylidene chloride/itaconic acid/alkyl acrylate copolymer layer and at least one colloid silver halide emulsion layer, said carboxylic acid being taken from the class consisting of aliphatic carboxylic acids of less than 6 carbon atoms, aromatic carboxylic acids of 7 carbon atoms and aralkyl acids of not more than 8 carbon atoms and such acids that contain at least one dipole group.

5. A photographic film comprising a polyethylene terephthalate film base having on one surface a layer comprising a Werner type chromium-carboxylic acid complex and a film-forming binding agent and on the other a thin layer of a vinylidene chloride/itaconic acid/alkyl acrylate copolymer layer, a gelatin layer and a gelatino silver halide emulsion layer, said carboxylic acid being taken from the class consisting of aliphatic carboxylic acids of less than 6 carbon atoms, aromatic carboxylic acids of 7 carbon atoms and aralkyl acids of not more than 8 carbon atoms and such acids that contain at least one dipole group.

6. A photographic film comprising a polyethylene terephthalate film base having on one surface a layer comprising a Werner type chromium-acetic acid complex, wherein said acid contains at least one dipole group, and a film-forming binding agent and on the other a thin layer of a vinylidene chloride/itaconic acid/alkyl acrylate copolymer layer and at least one colloid silver halide emulsion layer.

7. A photographic film comprising a polyethylene terephthalate film base having on one surface a layer comprising a Werner type chromium trichloroacetic acid complex and a film-forming binding agent and on the other a thin layer of a vinylidene chloride/itaconic acid/alkyl acrylate

11

copolymer layer and at least one colloid silver halide emulsion layer.

8. A photographic film comprising a polyethylene terephthalate film base having on one surface a layer comprising a Werner type chromium phenylacetic acid complex and a film-forming binding agent and on the other a thin layer of a vinylidene chloride/itaconic acid/alkyl acrylate copolymer layer and at least one colloid silver halide emulsion layer.

9. A photographic film comprising a polyethylene terephthalate film base having on one surface a layer comprising a Werner type chromium p-nitrophenylacetic acid complex and a film-forming binding agent and on the other a thin layer of a vinylidene chloride/itaconic acid/alkyl acrylate copolymer layer and at least one colloid silver halide emulsion layer.

10. A photographic film comprising a polyethylene terephthalate film base having on one surface a layer comprising a Werner type chromium

12

p-nitrobenzoic acid complex and a film-forming binding agent and on the other a thin layer of a vinylidene chloride/itaconic acid/alkyl acrylate copolymer layer and at least one colloid silver halide emulsion layer.

11. A photographic film comprising a polyethylene terephthalate film base having on one surface a layer comprising a Werner type chromium thioglycollic acid complex and a film-forming binding agent and on the other a thin layer of a vinylidene chloride/itaconic acid/alkyl acrylate copolymer layer and at least one colloid silver halide emulsion layer.

STANLEY HANCOCK PATTEN.

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