

[54] **PROTECTIVE LAYER FOR
PHOTOTHERMOGRAPHIC ELEMENTS**

[75] Inventors: **Fredrick L. Hamb**, Rochester; **Gary L. Hiller**, Hilton; **Albert W. Wise**, Rochester, all of N.Y.

[73] Assignee: **Eastman Kodak Company**, Rochester, N.Y.

[22] Filed: **Aug. 6, 1973**

[21] Appl. No.: **385,935**

[52] U.S. Cl. **96/48 HD**, 96/67, 96/87 R, 96/114, 96/114.1, 117/161 K, 260/47

[51] Int. Cl. **G03c 5/24**

[58] Field of Search 96/67, 50 PL, 114.1, 84 R, 96/87 R, 48 HD; 117/161 K; 260/47

[56] **References Cited**

UNITED STATES PATENTS

3,079,837	3/1963	Theilemann	96/84 R X
3,190,197	6/1965	Pinder	96/50 PL X
3,317,466	5/1967	Caldwell et al.	96/67 X
3,634,089	1/1972	Hamb	96/87 R
3,656,954	4/1972	Thiers et al.	96/67
3,657,185	4/1972	Wear	96/114.1 X

3,725,070	4/1973	Hamb et al.	96/87 R
3,769,264	10/1973	Wilson et al.	260/75 R
3,772,405	11/1973	Hamb	260/860
3,793,249	2/1974	Hamb et al.	260/47 C
3,803,096	4/1974	Wilson	260/75 R

Primary Examiner—Norman G. Torchin
Assistant Examiner—Alfonso T. Suro Pico
Attorney, Agent, or Firm—R. E. Knapp

[57] **ABSTRACT**

On a photographic element comprising at least one heat-processable, photographic layer, a protective layer comprising certain carboxylic polyesters provides improved resistance to abrasion and fingerprinting, resistance to reticulation and surface cracking without adversely affecting sensitometric properties of the photographic element upon processing. A latent image in such a photographic element can be developed by uniformly heating the photothermographic element containing the protective layer. Silica particles in the protective layer can enhance resistance of the protective layer to sticking to a heated metal surface and further enable the layer to glide smoothly over the heated metal surface.

12 Claims, No Drawings

PROTECTIVE LAYER FOR PHOTOTHERMOGRAPHIC ELEMENTS

BACKGROUND OF THE INVENTION

1 Field of the Invention

This invention relates to protective layers comprising certain film-forming carboxylic polyesters for photographic elements comprising at least one heat-processable, photographic layer said protective layers providing improved surface properties without adversely affecting sensitometric properties of the photographic element upon processing. In one of its aspects, it relates to photothermographic elements containing such improved protective layers. In another of its aspects it relates to a method of developing a latent image in a photothermographic element employing the described protective layer.

2. Description of the State of the Art

It is well known to employ protective layers, especially overcoat layers, on photographic elements and photothermographic elements. A commonly employed overcoat layer for photothermographic elements comprises cellulose acetate. Such overcoat layers are described, for example, in Belgian Pat. No. 729,043 and U.S. Pat. No. 2,732,304 issued Jan. 24, 1956. Photothermographic materials are also known as described, for example, in Belgian Pat. No. 765,452 issued May 28, 1971; Belgian Pat. No. 765,602 issued May 28, 1971; Belgian Pat. No. 765,601 issued May 28, 1971; Belgian Pat. No. 766,658 issued June 30, 1971; Belgian Pat. No. 766,590 issued June 15, 1971; Belgian Pat. No. 766,589 issued June 15, 1971; Belgian Pat. No. 768,071 issued July 30, 1971; U.S. Pat. No. 3,152,903 of Shepard et al., issued Oct. 13, 1964; U.S. Pat. No. 3,152,904 of Sorensen et al., issued Oct. 13, 1964 and U.S. Pat. No. 3,457,075 of Morgan et al., issued July 22, 1969. Photosensitive elements designed for processing with heat and which lack protective layers such as a protective overcoat layer, are especially susceptible to fingerprint marks and scratches which can become visible upon exposure to room-light handling and processing. Such photosensitive elements also are susceptible to abrasion marks, especially in machine processing wherein the photosensitive layer side of the element is contacted with a metal roller or the like. In addition, the processing of photothermographic elements by contacting the side of the photothermographic element containing the photosensitive layer with the heating means can cause surface cracking, reticulation, and bubbling which can detract from the overall image quality desired. An ethyl cellulose overcoat layer has not satisfactorily overcome these problems. It has also been proposed, as described in copending application Ser. No. 244,850 of Hiller and Hamb, filed Apr. 17, 1972, to employ certain polycarbonate polymers with silica particles in an overcoat for photographic materials. However, such polycarbonate compounds have been considered to be very expensive compared to such overcoat materials as ethyl cellulose.

Various matting agents have also been employed in

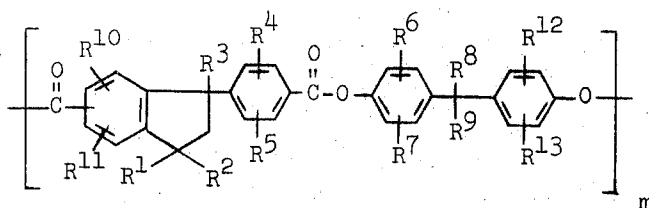
photosensitive materials. Such matting agents are described, for example, in British Pat. No. 692,592 published June 10, 1953; U.S. Pat. No. 3,411,907 of Whitmore et al., issued Nov. 19, 1968; and U.S. Pat. No. 3,022,169 of Heckelman issued Feb. 20, 1962. Silica has been employed as a matting agent and for other purposes in photosensitive materials. Matting agents alone, however, have not been found to provide an answer to the problems of protecting photosensitive materials especially photothermographic materials from undesired fingerprint marking, scratches and the like.

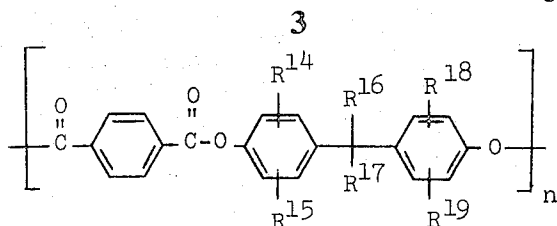
In the application of polymeric overcoats to photothermographic materials, it is necessary to employ polymers which are resistant to processing temperatures employed, such as temperatures above about 100°C. A polymer which has been found useful as a support material is poly(ethylene terephthalate). However, polymers which have been useful for support materials have not been found useful, as a class, for protective overcoat purposes because they do not satisfy one or more of the following characteristics: (1) they do not provide sufficient resistance to abrasion and fingerprint marking, (2) they do not sufficiently provide resistance to reticulation and surface cracking, (3) they do not provide sufficient resistance to surface bubbling, (4) they are not sufficiently soluble in common organic solvents to provide desired coating compositions on photosensitive layers employing hydrophobic polymeric binders, such as poly(vinyl butyral) polyesters, polycarbonates, and poly(vinyl ketals), and (5) they are not sufficiently transparent for desired viewing of an image. Accordingly, although there are many polymers that have resistance to high temperature decomposition, such as there are many polymers with so-called glass transition temperatures above about 190°C., these polymers, as a class, are not satisfactory for use as overcoats because other properties are required than the property of high glass transition temperature.

There has, accordingly, been a continuing need to provide improved protective layers, especially protective overcoat layers for photographic materials. This continuing need has been especially important to photothermographic materials, to provide the desired described properties such as resistance to abrasion, fingerprint marks, and undesired surface properties such as reticulation, surface cracking and surface bubbling, without adversely affecting sensitometric properties of the photographic element.

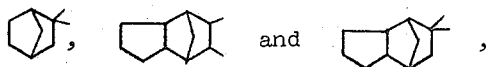
SUMMARY OF THE INVENTION

It has been found, according to the invention, that the described properties are provided in a photographic element, especially a photothermographic element, containing at least one heat-processable photographic layer, by a protective layer comprising a carboxylic polyester having a glass transition temperature of at least 190°C. having repeating units represented by the formula:

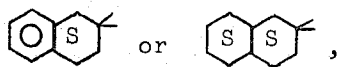




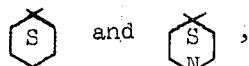
wherein m represents 15 to about 100 mole percent and n represents 0 to about 85 mole percent; R^1 and R^3 are each hydrogen atoms or alkyl containing 1 to 6 carbon atoms and preferably methyl; R^2 is alkyl containing 1 to 6 carbon atoms and preferably methyl; R^4 , R^5 , R^6 , R^7 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{18} and R^{19} are each hydrogen atoms; aryl, preferably aryl containing 6 to 12 carbon atoms, such as phenyl and naphthyl; halogen atoms, preferably chlorine or bromine atoms; nitro; cyano; and alkoxy, preferably alkoxy containing 1 to 4 carbon atoms, such as methoxy ethoxy, or propoxy; R^8 , R^9 , R^{16} and R^{17} are each hydrogen atoms; alkyl containing 1 to 6 carbon atoms, such as methyl and ethyl; cycloalkyl such as cyclohexyl; and aromatic radicals containing 6 to 20 carbon atoms, such as phenyl, 3,4-dichlorophenyl, 2,4-dichlorophenyl, or R^8 and R^9 , taken together with the carbon atom to which they are bonded can be a bridged ring moiety, such as containing up to 12 carbon atoms, for example,



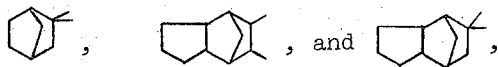
or a fused ring moiety, such as containing up to 12 carbon atoms, for example,



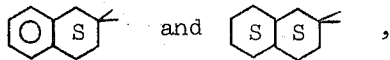
a monocyclic moiety or a heterocyclic moiety, such as



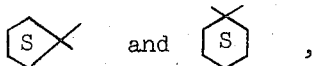
containing 4 to 7 atoms in the ring, or R^{16} and R^{17} taken together with the carbon atom to which they are bonded can be a bridged ring moiety such as



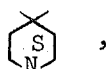
or a fused ring moiety, such as



or a monocyclic moiety such as



or a heterocyclic moiety, such as



containing 4 to 7 atoms in the ring.

Alkyl and aryl as employed herein include alkyl and aryl substituted with groups which do not adversely affect the properties of the described photothermographic materials. For example, alkyl includes substituted alkyl wherein the substituent group can be methyl

or ethyl or phenyl. Aryl, for instance, includes substituted aryl wherein the substituent group can be alkyl containing 1 to 3 carbon atoms, or can be phenyl. These carboxylic polyesters preferably have a glass transition temperature above that employed for processing of the photographic material. In some cases it can be desirable to employ silica particles such as silica particles having an average particle size of 0.001 to 0.10 micron in the protective layer to provide improved properties, such as enhanced resistance of the described protective layer to sticking to a heated metal surface and further enable the layer to glide smoothly over the heated metal surface.

Also, according to the invention a process is provided for developing an image in the described photographic element comprising a support having thereon at least one heat developable photographic layer and a protective overcoat layer comprising the described carboxylic polyester by uniformly heating the element, such as from about 80°C. to about 250°C. for a sufficient time to provide the desired developed image. This process can be carried out by contacting the photographic element with a suitable heating means to provide the described temperature.

DETAILED DESCRIPTION OF THE INVENTION

A range of carboxylic polyesters within the designated formula, having a glass transition temperature of at least 190°C., are useful in protective layers according to the invention. In photographic materials for processing with heat, a carboxylic polyester is useful which has a glass transition temperature greater than the processing temperature of the photographic material in order to prevent distortion of the protective layer during heating. Carboxylic polyesters within the described formula having a glass transition temperature above 190°C. are especially useful. The most useful carboxylic polyesters have a glass transition temperature above 200°C. and preferably above 220°C. Useful carboxylic polyesters have an average molecular weight of at least 10,000 and preferably from about 30,000 to 100,000. The molecular weight can be determined by methods known in the polymer art. Also, the glass transition temperatures as used herein, unless otherwise specified, can be determined by differential thermooanalysis as described in "Techniques and Methods of Polymer Evaluation," Volume I, Marcel Dekker, Inc., New York, 1966. Useful carboxylic polyesters are soluble in common organic coating solvents such as methylene chloride, chloroform, 1,1,2-trichloroethane, acetone, 2-pentanone, ethyl acetate and toluene, in order to facilitate application of a layer as described. Useful carboxylic polyesters are described, for example, in U.S. Pat. No. 3,634,089 of Hamb issued Jan. 11, 1972 and U.S. Pat. No. 3,657,185 of Wear issued Apr. 18, 1972.

The described carboxylic polyesters can be prepared employing procedures known in the art as described in U.S. Pat. No. 3,634,089 of Hamb issued Jan. 11, 1972. Generally, any of the known esterification procedures used in the polymer art is useful for making the described carboxylic polyesters. These include so-called interfacial procedures, solution procedures and ester interchange procedures known in the art.

Useful carboxylic polyesters are typically completely transparent and colorless when coated on a support. It is necessary, however, if the polymer is not completely

transparent that it at least be sufficiently transparent for desired viewing of an image in the photothermographic material.

While various methods known in the art can be employed for preparing the described carboxylic polyesters, typical reactants employed when preparing the polymers within the described generic structure wherein n is 0 are:

A. indan moiety:

1,1,1-trimethyl-5-carboxy-3-(p-carboxyphenyl)indan

1,3-diethyl-2-methyl-5-carboxy-3-(p-carboxyphenyl)indan

1,3-dibutyl-2-methyl-5-carboxy-3-(p-carboxyphenyl)indan, and

B. bis-phenol moiety

2,2-bis(4-hydroxyphenyl)propane

1-phenyl-1,1-bis(4-hydroxyphenyl)ethane

1,1-bis(4-hydroxyphenyl)cyclohexane

2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane

2,2-bis(3,5-dimethyl-4-hydroxyphenyl)-propane

For those polymers within the described generic structure wherein n is 1 to about 50 mole percent, a third moiety is employed in the polymerization which is terephthalic acid.

The described carboxylic polyesters have a glass transition temperature which is much higher than, for example, cellulose acetate. This property provides an advantage for photothermographic materials enabling the photothermographic materials to be processed at higher temperatures without formation of the described surface defects. In addition, the described carboxylic polyesters do not adversely affect the sensitometric properties of photothermographic materials such as minimum density, maximum density, photographic speed and the like, whereas cellulose acetate, a commonly employed overcoat causes changes in sensitometric behavior.

The concentration of carboxylic polyester which is useful in the protective layer of a photographic element, especially a photothermographic element, according to the invention can vary depending upon the particular photographic element, processing conditions, components in the photographic element, particular carboxylic polyester and the like. A useful concentration range is about 25 milligrams to about 400 milligrams of carboxylic polyester per 929 square centimeters of support of the photographic element. An especially useful concentration range, or coating coverage, of carboxylic polyester in a protective layer of a photothermographic element is about 75 milligrams to about 200 milligrams of carboxylic polyester per 929 square centimeters of support of the photothermographic element.

It is often useful to provide further increase in resistance of the protective layer to sticking to a heated metal surface and further enable the layer to glide smoothly over the heated metal surface, with certain of the described carboxylic polyesters by employing a matting agent, especially silica particles, in the protective layer. Silica particles having typically an average particle size range of 0.001 micron to 0.010 micron, preferably 0.005 micron to 0.05 micron are useful. Silica products for this purpose are available commercially such as silica sold under the trade name of Cab-O-Sil which is a registered trademark of Cabot Corporation, U.S.A. A useful silica product is colloidal silica

in the form of a dry powder which is mixed with the described carboxylic polyester before coating. This enables writing information on the photographic element with a pencil or ball-point pen after processing. Another useful product is "Syloid" which is a registered trademark of W. R. Grace Company, U.S.A.

The concentration of matting agent, especially silica, which is useful in a protective layer according to the invention can vary depending upon the particular photographic element, processing conditions, particular carboxylic polyester employed, and the like. A useful concentration range, or coating coverage, is about 2 milligrams to about 25 milligrams of silica per 929 square centimeters of support of the photographic element. In photothermographic elements an especially useful concentration range, or coating coverage, is about 5 milligrams to about 15 milligrams of silica per 929 square centimeters of the photothermographic element.

The described protective layer according to the invention can be employed with various photographic elements. Accordingly, one embodiment of the invention is: in a photographic element comprising a support having thereon at least one heat-processable, photographic layer and a protective layer, the improvement comprising as said protective layer a carboxylic polyester having a glass transition temperature of at least 190°C. having repeating units represented by the formula of the described generic structure. Especially useful carboxylic polyesters in this embodiment are copolymers of (i) 1,1,3-trimethyl-5-carboxy-3-(p-carboxyphenyl)indan, (ii) terephthalic acid and (iii) bisphenol A. Another especially useful carboxylic polyester according to this embodiment is a copolymer of (i) 1,1,3-trimethyl-5-carboxy-3-(p-carboxyphenyl)indan and (ii) bisphenol A. This latter polymer is especially useful in combination with the described silica particles to provide improved resistance to reticulation.

The term "bisphenol A" as employed herein refers to the compound 4,4'-isopropylidene diphenol also known as 2,2-(para-hydroxyphenyl)propane and 2,2-bis(4-hydroxyphenyl)propane.

A preferred embodiment of the invention is one in which the described photographic layer comprises:

1. an oxidation-reduction image-forming combination comprising
 - i. a silver salt oxidizing agent with
 - ii. an organic reducing agent,
2. photosensitive silver halide,
3. a polymeric binder, and
4. a so-called activator-toning agent, also known as a toner.

The photosensitive layers and other layers of an element according to the invention and described herein can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polystyrene film, poly(ethylene terephthalate) film, poly(ethylene 2,6-naphthalene dicarboxylate), polyesters of 1,1,3-trimethyl-3-(p-carboxyphenyl)-5-carboxyindan and bisphenols as described in U.S. Pat. No. 3,634,089 issued Jan. 11, 1972, polycarbonate film and related films or resinous materials, as well as glass, paper, metal and the like. Typically a flexible support is employed, such as a paper support which can be partially acetylated or coated with baryta and/or an alpha-olefin polymer such as a polymer of an alpha-olefin contain-

ing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylene-butene copolymers and the like.

The photographic elements according to the invention, especially photothermographic elements, contain a photosensitive component. The photosensitive component is typically a photosensitive silver salt or complex, such as photosensitive silver halide or a complex of silver with an organic compound such as a silver dye complex. The photosensitive silver halide is especially useful as a photosensitive component because of its high photosensitivity. A typical concentration of photosensitive component in a photothermographic element according to the invention is about 0.005 to about 0.50 moles of photosensitive component per mole of oxidizing agent in the photothermographic element. Especially useful photosensitive silver halides include silver chloride, silver bromide, silver bromiodide, silver chlorobromiodide, or mixtures thereof. The photosensitive silver halide can be coarse or fine-grain, very fine-grain silver halide being especially useful. The photosensitive silver halide can be prepared by any of the procedures known in the photographic art. Such procedures and forms of photosensitive silver halide are described, for example, in the Product Licensing Index, Volume 92, December, 1971, publication 9232, pages 107-110, paragraph I.

The photosensitive silver halide employed according to the invention can be unwashed or washed, can be chemically sensitized, can be protected against the production of fog and stabilized against loss of sensitivity during keeping, as described in the above Product Licensing Index reference.

Photographic elements according to the invention can contain development modifiers that function as speed-increasing compounds, developing agents, hardeners, antistatic layers, plasticizers and lubricants, coating aids, brighteners, spectral sensitizing dyes, absorbing and filter dyes, also as described in the above Product Licensing Index reference, pages 107-110.

The described photothermographic elements can comprise an oxidation-reduction image-forming combination which contains an oxidizing agent, typically a heavy metal salt oxidizing agent. The heavy metal salt oxidizing agent can be a heavy metal salt of an organic acid such as a fatty acid which is resistant to darkening upon illumination. An especially useful class of heavy metal salts or organic acids is represented by the water insoluble silver salts of long-chain fatty acids which are stable to light. Compounds which are suitable silver salt oxidizing agents include silver behenate, silver stearate, silver oleate, silver laurate, silver hydroxystearate, silver caprate, silver myristate and silver palmitate. Silver salts can be employed as the silver salt oxidizing agents which are not silver salts of long-chain fatty acids. Such silver salt oxidizing agents which are useful according to the invention include, for example, silver benzoate, silver benzotriazole, silver terephthalate, silver phthalate, and the like. Oxidizing agents which are not silver salts can be employed if desired such as gold stearate, mercury behenate, gold behenate, and the like, but silver salts are preferred. Combinations of the described oxidizing agents can be employed if desired.

Reducing agents which can be employed in the described oxidation-reduction image forming combination include, for example, substituted phenols and naphthols, for example, bis- β -naphthols. Suitable bis- β -naphthols include, for example, 2,2'-dihydroxy-1,1'-

binaphthyl, 6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthyl, 6,6'-dinitro-2,2'-dihydroxy-1,1'-binaphthyl and/or bis-(2-hydroxy-1-naphthyl)methane. Other reducing agents which can be employed in photographic elements according to the invention include polyhydroxybenzenes such as hydroquinone silver halide developing agents, e.g., hydroquinone, alkyl-substituted hydroquinones such as tertiary butyl hydroquinone, methyl hydroquinone, 2,5-dimethyl hydroquinone and 2,6-dimethyl hydroquinone; catechols and pyrogallols; chloro-substituted hydroquinones such as chloro hydroquinone or dichloro hydroquinone; alkoxy-substituted hydroquinone such as methoxy hydroquinone or ethoxy hydroquinone; aminophenol developing agents, such as 2,4-diaminophenols and methylaminophenols; ascorbic acid developing agents such as ascorbic acid, ascorbic acid ketals and ascorbic acid derivatives; hydroxylamine developing agents; 3-pyrazolidone developing agents such as 1-phenyl-3-pyrazolidone and 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone and the like. Reducing agents which are also useful include sulfonamidophenols as described in pending U.S. application Ser. No. 272,832 of Evans and McLaen, filed July 18, 1972 and now U.S. Pat. No. 3,801,231. Combinations of the described reducing agents can be employed if desired.

It is often desirable to employ a so-called activator-toning agent in the photothermographic elements according to the invention to obtain a desired image. The activator-toning agent is typically useful in a range of concentration, such as a concentration of about 0.10 moles to about 1.1 moles of activator-toning agent per mole of oxidizing agent in the photothermographic element. A typical suitable activator-toning agent is a heterocyclic activator-toning agent containing at least one nitrogen atom as described in Belgian Pat. No. 766,590 issued June 15, 1971. Typical activator-toning agents include, for example, phthalimide, N-hydroxyphthalimide, N-potassium phthalimide, N-silver phthalimide, N-mercury phthalimide, succinimide, N-hydroxynaphthalimide, and/or N-hydroxysuccinimide. Other activator-toning agents which can be employed include phthalazinone, 2-acetylphthalazinone, and the like.

It is desirable in some cases to employ an image stabilizer and/or image stabilizer precursor in the described elements of the invention. Typical image stabilizers or stabilizer precursors are described, for example, in Belgian Pat. No. 768,071 issued July 30, 1971. Typical stabilizer precursors include, for example, azothioethers and blocked azole thione stabilizer precursors as described in this Belgian patent and the stabilizers described in U.S. Pat. No. 3,707,377 issued Dec. 26, 1972.

A photographic element, especially a photothermographic element, as described according to the invention can contain various colloids alone or in combination as vehicles, binding agents and in various layers, including the described protective layer. Suitable materials can be hydrophobic or hydrophilic depending on the particular means of processing employed. They are transparent or translucent and include both naturally-occurring substances such as proteins, for example, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water soluble polyvinyl compounds like poly(vinyl pyrrolidone), ac-

rylamide polymers and the like. Other synthetic polymeric compounds which can be employed include dispersed vinyl compounds such as in latex form and particularly those which increase dimensional stability of photographic materials. Effective polymers include water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates, methacrylates and those which have cross-linking sites which facilitate hardening or curing as well as those having recurring sulfobetaine units as described in Canadian Pat. No. 774,054. Especially useful high molecular weight materials and resins include poly(vinyl butyral), cellulose acetate butyrate, polymethyl methacrylate, poly(vinyl pyrrolidone), ethylcellulose, polystyrene, poly(vinyl chloride), chlorinated rubber, polyisobutylene, butadiene-styrene copolymers, vinyl chloride-vinyl acetate copolymers, copolymers of vinyl acetate, vinyl chloride and maleic acid and polyvinyl alcohol.

If desired, the photosensitive silver halide employed in the described photothermographic elements can be prepared *ex situ*, that is, away from other components of the photothermographic material, and/or *in situ*, that is in with components of the described materials. The photosensitive silver halide can be prepared *in situ* such as described in U.S. Pat. No. 3,457,075 of Morgan et al., issued July 22, 1969.

The photosensitive layers and other layers according to the invention can be coated by various coating procedures including dip coating, air knife coating, curtain coating or extrusion coating using hoppers such as described in U.S. Pat. No. 2,681,294 of Beguin issued June 15, 1954. If desired, two or more layers can be coated simultaneously such as described in U.S. Pat. No. 2,761,791 of Russell issued Sept. 4, 1956 and British Pat. No. 837,095.

Spectral sensitizing dyes can be used in the described photographic elements and photothermographic elements of the invention to confer additional sensitivity to the elements of the invention. Useful sensitizing dyes are described, for example, in the Product Licensing Index, Vol. 92, December, 1971, publication 9232, pages 107-110, paragraph XV.

Photographic elements according to the invention containing the described protective layer can be processed by various methods including processing in alkaline solutions containing conventional developing agents and by processing by other means as described in the Product Licensing Index, Vol. 92, December, 1971, publication 9232, pages 107-110, paragraph XXIII.

The protective layers employed according to the invention can be provided in elements designed for color photography, for example, elements containing color-forming couplers or elements to be developed in solutions containing color-forming couplers; or in so-called false sensitized color materials such as described in U.S. Pat. No. 2,763,549 of Hansen issued Sept. 18, 1956.

After exposure of the described photothermographic element according to the invention, the resulting latent image can be developed merely by heating the element to moderately elevated temperatures. This merely involves heating the described photothermographic element overall to about 80°C. to about 250°C. such as for about 0.5 seconds to about 60 seconds. By increasing or decreasing the length of time of heating, a higher or lower temperature within the described range can be

employed depending upon the desired image. A developed image is typically produced within several seconds, such as about 0.5 seconds to about 60 seconds.

Any suitable means can be used for providing the desired processing temperature range. The heating means can be, for example, a simple hot plate, iron or roller; or hot air convection means; or dielectric heating means. As described, the photothermographic element containing the protective layer of the invention can be contacted with the heating means with the protective layer contacting the heating means directly.

If desired, one or more components of the photographic element, or photothermographic element, can be in one or more layers of the element. For example, in some cases it can be desirable to include certain percentages of the reducing agent, activator-toner, image stabilizer and/or stabilizer precursor in the described protective layer. This can reduce migration of certain addenda throughout the layers of the element.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

A photothermographic element is prepared as follows:

A silver behenate dispersion, designated as dispersion A, is prepared by ball-milling the following components for 72 hours:

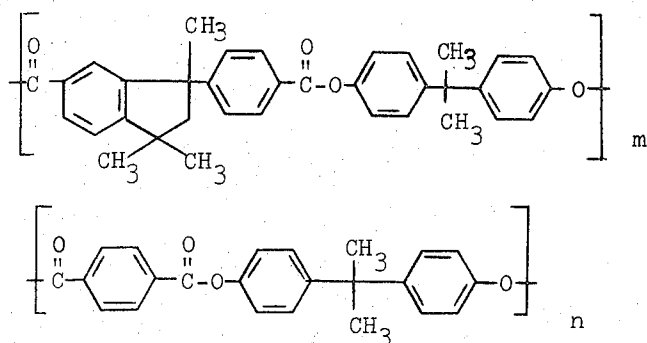
silver behenate	168 g.
behenic acid	128 g.
poly(vinyl butyral)	120 g.
phthalimide	34 g.
acetone-toluene (1:1 by volume)	2 liters

After ball-milling, 300 ml. of an acetone solution containing 1% by weight lithium bromide is added to the resulting dispersion which is then mixed thoroughly for 16 hours.

A photothermographic composition is prepared by combining 639 ml. of dispersion A with the following components in the order indicated:

acetone-methanol solution (33:1 by volume) containing 0.1% by weight 3-carboxymethyl-5-[(3-methyl-2-thiazolidinylidene)-1-methylethylidene]-rhodanine	18.0 ml.
acetone containing 10% by weight 2,2'-dihydroxy-1,1'-binaphthyl	149.0 ml.
acetone containing 10% by weight 2,4-dihydroxybenzophenone	22.5 ml.
acetone containing 1% by weight 5-acetyl-2-benzoyloxycarbonylthio-4-methylthiazole	72.0 ml.
acetone-toluene (1:1 by volume)	225 ml.

This photothermographic composition is coated at 6.0 g. of photothermographic composition per 929 square centimeters on a paper support. The coverage corresponds to 6.46 mg. of silver per dm². After the coating is dry, the resulting photothermographic element is overcoated with a dichloromethane-methanol solution (19:1 by volume) containing 5% by weight of a copolymer of (i) 1,1,3-trimethyl-5-carboxy-3-(p-carboxyphenyl) indan, (ii) terephthalic acid and (iii) bisphenol A. This copolymer has a glass transition temperature of 240°C. and is represented by the formula:



wherein m is 40 mol percent and n is 60 mol percent. The solution is overcoated onto the photothermographic element at 0.43 grams of the solution of copolymer per dm^2 which corresponds to 10.76 mg. of copolymer per dm^2 . The overcoat is permitted to dry to provide a transparent, adherent coating. The overcoated photothermographic element is then imagewise exposed for 1 second to tungsten light to provide a latent image. The latent image is developed by uniformly heating the element by holding the side of the element opposite the overcoat layer against a heated metal block at 160°C . for 4 seconds. A neutral, (jet black) developed image having a beige background results.

The resulting, overcoated photothermographic element is not susceptible to fingerprint marks and abrasion, exhibits no surface cracking or reticulation, and exhibits no surface bubbling.

The glass transition temperature (T_g) of the copolymer employed as the overcoat is 240°C . The copolymer is amorphous and is more than 5% by weight soluble in organic solvents such as methylene chloride, chloroform, 1,1,2-trichloroethane, acetone, 2-pentanone, ethyl acetate and toluene. No adverse sensitometric effects are observed in the photothermographic element as a result of the copolymer overcoat.

EXAMPLE 2

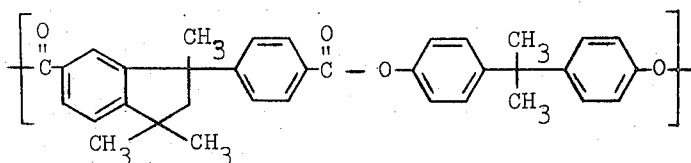
This is a comparative example.

The procedure set out in Example 1 is repeated with the exception that the photothermographic element is not overcoated with the described copolymer of Example 1.

The resulting developed image is neutral (jet black) with a beige background. However, the element is susceptible to abrasion and fingerprinting which becomes visible upon room-light exposure, such as after 1 week storage under 80-foot candles of light and 80% relative humidity.

EXAMPLE 3

The procedure set out in Example 1 is repeated with the exception that a polyester of (i) 1,1,3-trimethyl-5-carboxy-3-(p-carboxyphenyl)indan and (ii) bisphenol A is employed as the overcoat in place of the copolymer described in Example 1. The designated polyester has a glass transition temperature of 265°C . and is represented by the formula:



Results similar to Example 1 are observed.

EXAMPLE 4

The procedure set out in Example 3 is repeated except that the overcoat side of the imagewise exposed photothermographic element is contacted with the described, heated metal block at 150°C . for 4 seconds.

Results are observed similar to those observed for Example 3 except that some reticulation (also known as crazing) is observed in the overcoat after the described heating.

EXAMPLE 5

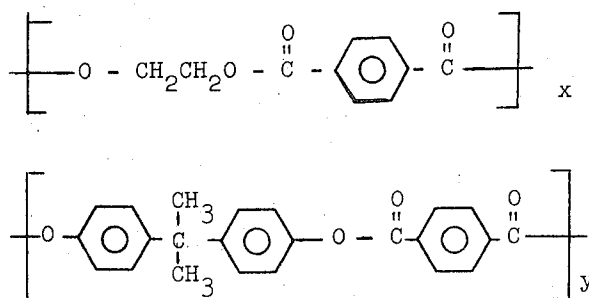
The procedure set out in Example 4 is repeated except that silica particles are mixed with the described polyester before overcoating the photothermographic element to provide an overcoat containing 10 mg. of silica per 929 square centimeters of support. The silica particles have an average particle size of 0.001 to 0.10 microns.

Results are observed similar to those of Example 4 except that no reticulation is observed in the overcoat after the described heating.

EXAMPLE 6

This is a comparative example.

The procedure set out in Example 1 is repeated except that a copolymer (T_g is 127°C .) represented by the formula:



wherein x is 60 mol percent and y is 40 mole percent, is employed in place of the copolymer described in Example 1, and with the exception that the overcoat side of the imagewise exposed photothermographic element

13

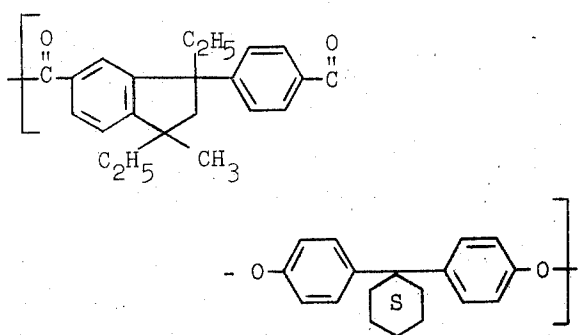
is contacted with the described, heated metal block at 150°C. for 4 seconds.

Results similar to Example 1 are observed except that the overcoat is susceptible to abrasion and fingerprint marks and is very soft compared to the overcoat of Example 1.

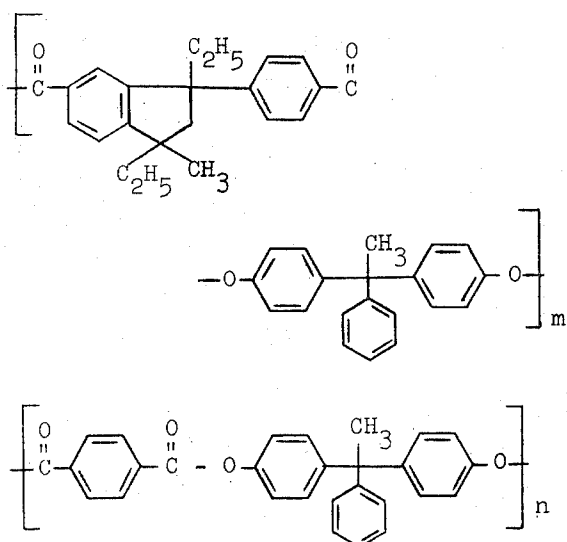
EXAMPLES 7-13

Other copolymers employed as overcoats for abrasion resistance as in Example 1 are as follows:

EXAMPLE 7

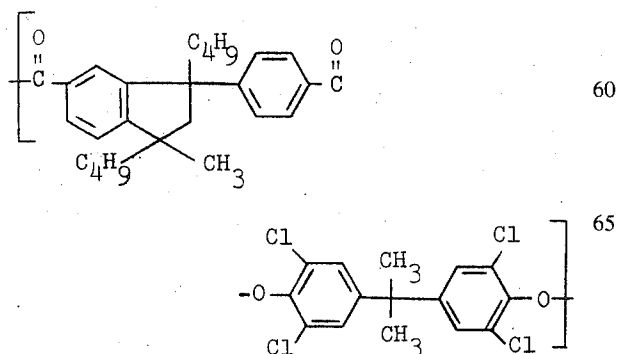


EXAMPLE 8



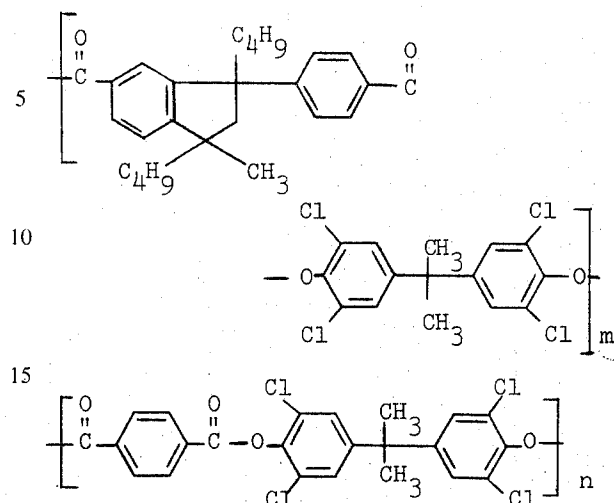
wherein m is 50 mole percent and n is 50 mole percent.

EXAMPLE 9



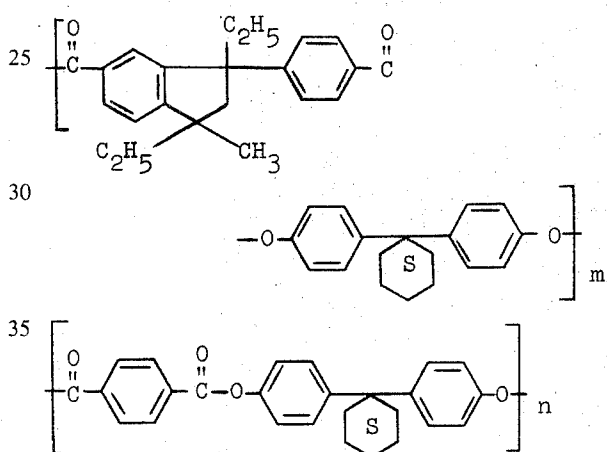
14

EXAMPLE 10



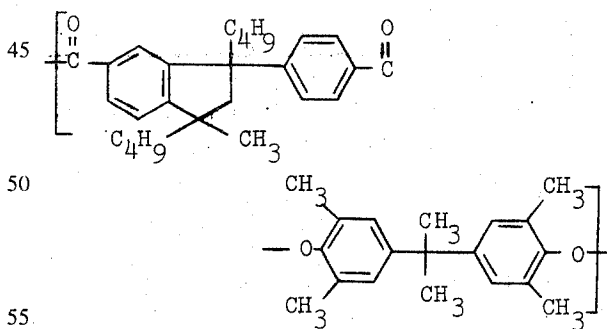
wherein m is 40 mole percent and n is 60 mole percent.

EXAMPLE 11

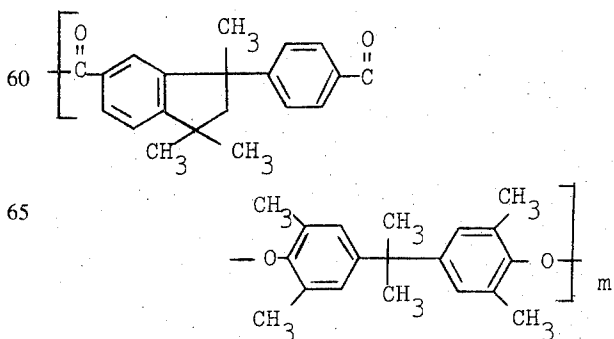


wherein m is 20 mole percent and n is 80 mole percent.

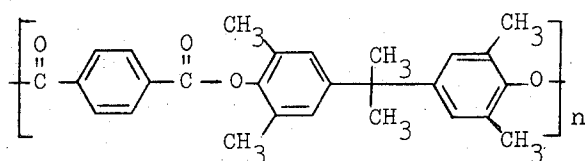
EXAMPLE 12



EXAMPLE 13



15

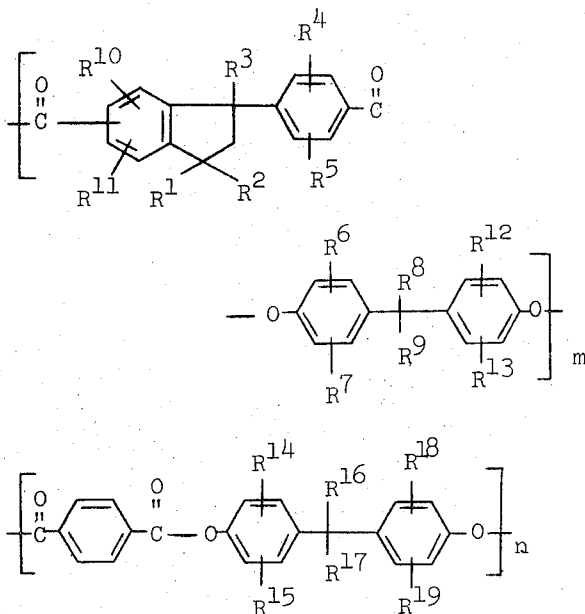


wherein m is 50 mole percent and n is 50 mole percent.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

What is claimed is:

1. In a photothermographic element having a protective layer, the improvement comprising as said protective layer a carboxylic polyester having a glass transition temperature of at least 190°C. having repeating units represented by the formula:



wherein m represents 15 to about 100 mole percent and n represents 0 to about 85 mole percent;

R^1 and R^3 are each hydrogen atoms or alkyl groups containing 1 to 6 carbon atoms; R^2 is alkyl containing 1 to 6 carbon atoms;

R^4 , R^5 , R^6 , R^7 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{18} and R^{19} are each hydrogen atoms; aryl containing 6 to 12 carbon atoms; halogen atoms; nitro; cyano; and alkoxy containing 1 to 4 carbon atoms;

R^8 , R^9 , R^{16} and R^{17} are each hydrogen atoms; alkyl containing 1 to 6 carbon atoms; cycloalkyl; and aromatic radicals containing 6 to 20 carbon atoms, or R^8 and R^9 , taken together with the carbon atom to which they are bonded can be a bridged ring moiety, a fused ring moiety, a monocyclic moiety, or a heterocyclic moiety containing 4 to 7 carbon atoms in the ring, and R^{16} and R^{17} , taken together with the carbon atom to which they are bonded can be a bridged ring moiety, a fused ring moiety, a monocyclic moiety or a heterocyclic moiety containing 4 to 7 carbon atoms in the ring.

2. A photothermographic element as in claim 1

16

wherein said carboxylic polyester is a copolymer of (i) 1,1,3-trimethyl-5-carboxy-3-(p-carboxyphenyl)indan, (ii) terephthalic acid and (iii) bisphenol A.

3. A photothermographic element as in claim 1 wherein said carboxylic polyester is a copolymer of (i) 1,1,3-trimethyl-5-carboxy-3-(p-carboxyphenyl)indan and (ii) bisphenol A.

4. A photothermographic element as in claim 1 wherein said protective layer comprises about 1 mg. to about 100 mg. of said carboxylic polyester per square decimeter of support.

5. A photothermographic element as in claim 1 also comprising silica particles.

6. A photothermographic element as in claim 1 also comprising 2 mg. to 25 mg. of silica particles having an average particle size of 0.001 to 0.10 micron per 929 square centimeters of support.

7. A photothermographic element having thereon a protective layer as in claim 1 wherein said photothermographic element comprises a support and

I. an oxidation-reduction image-forming combination comprising (i) a silver salt oxidizing agent with (ii) an organic reducing agent,

II. photosensitive silver halide,

III. a polymeric binder, and

IV. an activator-toning agent.

8. In a photothermographic element comprising a support and

a. an oxidation-reduction image-forming combination comprising (i) silver behenate with (ii) a sulfonamidophenol reducing agent,

b. photosensitive silver halide,

c. a poly(vinyl butyral) binder, and

d. an activator-toning agent comprising N-hydroxynaphthalimide, and

a protective layer the improvement wherein said protective layer is a copolymer of (i) 1,1,3-trimethyl-5-carboxy-3-(p-carboxyphenyl)indan and (ii) bisphenol A, said copolymer having a glass transition temperature of at least 190°C.

9. A photothermographic element as in claim 8 wherein said protective layer contains 2 mg. to 25 mg. of silica particles having an average particle size of 0.001 to 0.10 micron per square foot of support.

10. In a photothermographic element comprising

a. an oxidation-reduction image-forming combination comprising (i) silver behenate with (ii) a sulfonamidophenol reducing agent,

b. photosensitive silver halide,

c. a poly(vinyl butyral) binder, and

d. an activator-toning agent comprising N-hydroxynaphthalimide, and

a protective layer, the improvement wherein said protective layer is a copolymer of (i) 1,1,3-trimethyl-5-carboxy-3-(p-carboxyphenyl)indan, (ii) terephthalic acid, and (iii) bisphenol A, said copolymer having a glass transition temperature of at least 190°C.

11. A process of developing an image in a photothermographic element having thereon a protective overcoat layer comprising a carboxylic polyester as defined in claim 1 comprising heating said element from about 80°C. to about 250°C.

12. A process as in claim 9 wherein said heating is carried out for about 0.5 to about 60 seconds.

* * * * *