

1

3,529,963

IMAGE-YIELDING ELEMENTS AND PROCESSES
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U.S. Cl. 96—50

8 Claims

ABSTRACT OF THE DISCLOSURE

Image-yielding elements comprising (a) a silver salt of a highly fluorinated alkanesulfonic acid or dodecahydridecarboric acid, said acids having a pKa no greater than 2, (b) a photosensitizer which may be a photoreducible dye capable under actinic radiation of decomposing said salt to liberate the acid, (c) a hydrogen abstractable material, and (d) a polymer binder, and optionally (e) an acid-sensitive material preferably an aldehyde precursor and/or (f) water or a water-yielding material; and processes of image formation by exposing the elements to actinic radiation and heating them to form an image.

This application is a continuation-in-part of my prior application Ser. No. 468,977 filed July 1, 1965 and entitled Image-Yielding Elements and Processes (now abandoned).

This invention relates to new photographic image-forming elements and to a new process of image formation.

The conventional photographic process has been widely used to produce copies of original matter. This process has yielded high quality reproductions but has been time consuming and expensive since various steps of photographic processing are involved, e.g., exposing, developing, fixing, washing and drying. More rapid processes of image reproduction have been developed such as thermography, electrostatic image reproduction, etc. but these processes are more suited for copying simple images such as a printed text or a line drawing. These latter processes are not generally capable of making copies which even approach the high quality of those copies made by the conventional, wet photographic process. Furthermore, the rapid, dry processes often require elaborate and expensive equipment and the light sensitivity of the elements employed in such processes is relatively low.

An object of this invention is to provide a process capable of forming high quality images by simple, rapid and dry processing and requiring only simple and inexpensive equipment. A more specific object is to provide a process which can produce images having very high transmission optical densities on a fog free background. A further object includes the formation of high resolution, very fine grain images from relatively high speed photographic elements. A still further object is to provide simple and dependable elements for use in the process. Still further objects will be apparent from the following description of the invention.

The novel image-yielding elements of this invention have an image-forming layer comprising:

(a) A silver salt of a perfluoroalkanesulfonic or beta-hydroperfluoroalkanesulfonic acid,

(b) A photosensitizer capable, upon absorption of actinic radiation, of decomposing said silver salt to liberate a strong acid,

(c) A hydrogen abstractable material or compound which is a hydrogen donor for said photosensitizer during its absorption of actinic radiation,

(d) A carrier, preferably a film forming organic poly-

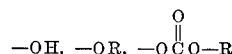
2

mer binder free from substantial amounts of labile covalent halogen, and optionally

(e) An acid-sensitive organic material which produces a color change in the presence of a strong acid (i.e., an acid having a pKa no greater than 2.0), said color change being sufficient to form a visible image, and/or

(f) Water or a water-yielding material or compound. Preferably, the organic material (e) contains a plurality of units of the structure

wherein X is

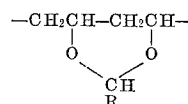


or halogen, wherein R is alkyl or aryl, and wherein H—X is readily removable from the unit in exposed areas to cause the above change in color sufficient to form a visible image.

Component (b) may be a photoreducible ketone, e.g., a quinone, an alpha-diketone; or a photocleavable compound such as benzpinacolone, a polychlorinated biphenyl or bromonaphthalene which, upon irradiation, liberates a strong acid.

The photosensitizer may also be a photoreducible dye in the presence of a mild reducing agent which has a reduction potential less than that necessary to reduce the dye or metal salt in the absence of actinic radiation. Suitable photoreducible dyes are disclosed in Oster, U.S. 2,875,047 (Feb. 24, 1959).

Component (e), the acid-sensitive material, is preferably an aldehyde precursor hydrolyzable to an aldehyde by a strong acid. In the particularly preferred embodiment, component (e) is a polymeric acetal which contains intralinear units of the structure



where R is H or $\text{CH}_3\text{CH}_2\text{CH}_2-$, and which can also function as a hydrogen abstractable compound (c), as a water-yielding material (f), and a binder (d). When component (e) is polymeric it should form strong coherent films and act as a binder. The polymeric acetal may either have the acetal groups present as pendent groups on a polymeric backbone or may contain the acetal groups as part of a linear polymer chain.

The hydrogen abstractable compound (c) can, as disclosed above, be supplied by the organic polymer binder (d). Component (c) can also be a separate component such as an alcohol, or acetal. Component (c) which can also be designated as a hydrogen donor compound may be diethylene glycol and its monomethyl ether or diacetic acid ester, a polyethylene glycol of molecular weight 400–6000, or tetraethyl malondialdehyde acetal.

With regard to component (d), the polymeric binder should be free from labile, covalent halogen and preferably free from basic groups. Suitable classes and specific binders are listed in Burg et al. U.S.P. 3,060,023. Non-thermoplastic binders can be made thermoplastic by addition of a suitable plasticizer, e.g., dibutyl phthalate, tricresyl phosphate, etc. In some instances a single compound may serve two or more functions as listed above.

Component (f) when not water can be a hydrated material such as pinacol hydrate. Water can be produced by the acid catalyzed dehydration of hydroxy compounds such as pinacol or from a material serving some other function, e.g., from a polyvinyl acetal (e) if it is not completely acetalized.

3

The process of this invention comprises

(1) exposing, imagewise, to actinic radiation (preferably radiation predominating in wavelengths in the ultra-violet and visible regions of the spectrum) an image-yielding element having an image-forming layer containing components (a), (b), (c), (d) and, if desired, components (e) and (f), that are described above, to form a colored image in said stratum; and

(2) uniformly heating the exposed stratum to a temperature between 60 and 200° C., preferably from 100 to 170° C. to effect the dry development of a metal-containing image. The heating time may vary from a few seconds to five minutes or more with shorter exposure times requiring higher temperatures and vice versa. Also, as the amount of exposure in step (1) is increased, the time and/or temperature of the heating may be reduced. Steps (1) and (2) may be combined in a single step if the source of radiation also produces appreciable heat, e.g., a carbon arc. Optionally there is added a step (3) of fixing or stabilizing the developed image, e.g., by (a) complete wash-out of the unexposed image areas or (b) thermal transfer of the unexposed image areas to a separate, receptive support, followed by re-exposure and/or reheating of the transferred image. Still other methods of stabilizing the image can be employed, e.g., partial washout by using a solvent system that removes the metallic salt (a) and/or the photosensitizer (b) or by dusting or stripping techniques disclosed in U.S.P. 3,060,024 and 3,060,025.

In stabilizing the image by such processes as washout or thermal transfer, the process can be controlled to yield either a positive or a negative image by selection of the binder. For example, a polymeric acetal in which the acetal groups are pendent on a polymeric backbone can be imagewise cross-linked so that the unexposed areas are removable by washout or by thermal transfer. On the other hand, a linear polymeric acetal can be imagewise depolymerized to become removable in the exposed areas by washout or thermal transfer.

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

EXAMPLE I

A photosensitive binder solution was prepared as follows:

Polyvinyl formal¹ (15% by wt. soln. in 40 ethanol/60 toluene by wt.)—15.0 g.
 $\text{CF}_3\text{CHF}(\text{CF}_2\text{SO}_3\text{Ag})$ ²—0.5 g.
 9,10-phenanthrenequinone—0.13 g.
 Dioxane—40 ml.

The solution was coated on various film bases including polyethylene terephthalate (the resin subbed base described in Example IV of U.S.P. 2,779,684), paper, and aluminum and allowed to air dry. The photosensitive layer was exposed for 5 seconds at a distance of 12 inches through a letter text photographic negative to the radiation of a high-intensity photolight (Sylvania "Sun Gun"—Model SG 60, Lamp Type DXN). Later heating the layer to 150° C., in less than 1 minute effected the dry development of a black image. In a similar manner a copy was obtained using a halftone photographic negative. By exposing through a 21-step continuous tone photographic step tablet having an approximate density range of 0.25 to 3.05 it was possible to read out at least five steps.

Fixing to obtain stable images was accomplished (with

¹ Formvar® 7/95 S (Shawinigan Chemicals, Inc.), polyvinyl formal of molecular weight of 16,000–20,000, hydroxyl content of 7.0–9.0 (expressed as percent polyvinyl alcohol), acetate content of 9.5–13.0 (expressed as percent polyvinyl acetate), formal content of 80 (expressed as percent polyvinyl formal and having a specific gravity of 1.229.

² B-hydroperfluoroalkanesulfonic acids are prepared by the addition of sodium bisulfite to perfluoro-olefins in the presence of a buffer such as borax. See for example, Kosher et al., J. Am. Chem. Soc., 75, 4595 (1953). The salts can be made from the acids by conventional methods of neutralization with a base or by double decomposition.

4

equally satisfactory results) by washing in water and by dissolving out the unexposed areas with dioxane.

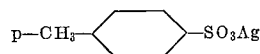
In other experiments, it was determined that the amount of silver salt in the above composition could be reduced to 0.1 g. with satisfactory results but with somewhat lower transmission optical densities.

EXAMPLE II

Example I was essentially repeated except that the 9,10-phenanthrenequinone photosensitizer was replaced by other quinone-type compounds including 1,4-naphthoquinone, 1,2-naphthoquinone, 2-methyl-1,4-naphthoquinone, retenequinone, anthraquinone, 2-methylanthraquinone, 2-ethylanthraquinone, 2-t-butylanthraquinone, 1,6-pyrenequinone, 3-nitro-1,2-naphthoquinone, thymoquinone and bianthrone. Similar results were also obtained when photosensitizers other than quinones were used such as furil (an α -diketone) and photocleavable compounds such as benzpinacolone and a mixture of various polychlorinated biphenyl compounds³ averaging about 3 atoms of chlorine per molecule.

EXAMPLE III

Example I was essentially repeated except that



and a 50/50, by weight, mixture of



and $\text{CF}_3\text{CHF}(\text{CF}_2\text{SO}_3\text{Ag})$ were used in place of



Similar results were obtained with the silver salt while the metal salt mixture was particularly useful in giving the high sensitivity associated with the silver salt along with the cross-linking of the polyvinyl formal binder in the exposed areas which was caused by the copper salt. This cross-linking made it possible to fix or stabilize more efficiently.

EXAMPLE IV

Example I was essentially repeated except that 0.5 g. of pinacol hydrate was added and the heat development was found to be effective at lower temperatures, e.g., 70 to 90° C.

EXAMPLE V

A photosensitive solution was prepared as follows:

Polymethyl methacrylate ¹ -methyl ethyl ketone	G.
(20% by wt. solution) -----	10.0
$\text{CF}_3\text{CHF}(\text{CF}_2\text{SO}_3\text{Ag})$ -----	0.5
Pinacol hydrate -----	0.5
Tetraethyl malondialdehyde acetal -----	0.5
1,4-naphthoquinone -----	0.1

¹ A low molecular weight polymer with an inherent viscosity of 0.20 for a solution containing 0.25 g. polymer in 50 ml. chloroform at 20° C.

The above solution was coated on a 0.002-inch polyethylene terephthalate film support and allowed to air dry. Exposing the photosensitive layer to actinic radiation as in Example I and subsequent heating of the exposed layer to 120° C. effected the dry development of a visible image.

A similar solution was prepared in the absence of the polymethyl methacrylate binder using a small quantity of the methyl ethyl ketone solvent. The solution was coated on a porous paper support, exposed and heat developed to give a similar image.

EXAMPLE VI

Example I was essentially repeated except that the poly-

³ Monsanto's "Aroclor" 1242 having a refractive index at 20° C. of 1.627–1.629, a density of 11.50 (lbs. per gal. at 25° C.), a boiling point of 325–366° C. (760 mm. Hg) and a pour point of -19° C. (ASTM D-97).

vinyl formal binder of that example was replaced with other polymeric acetals such as various polyvinyl butyral polymers which are commercially available. These included a polyvinyl butyral polymer of molecular weight 45,000–55,000, an hydroxyl content of 9.0–13.0 (expressed as percent polyvinyl alcohol), an acetate content of 0–2.5 (expressed as percent polyvinyl acetate), a butyral content of 88 (expressed as percent of polyvinyl butyral), and a specific gravity of 1.083 (Shawinigan Chemicals, Inc. Butvar® B-76). Results were similar to those obtained in Example I.

EXAMPLE VII

A photosensitive mixture was prepared from the following ingredients:

Butyl benzyl phthalate—0.4 g.
Phenanthrenequinone—0.06 g.
Tri-n-heptylamine (1 mg. per ml. in acetone solution)—10 ml.
 $\text{CF}_3\text{CHFCF}_2\text{SO}_3\text{Ag}$ —0.06 g.
Acetone—1 ml.
Polyvinyl butyral (described in Example VI)—1.33 g.

This mixture was applied to 0.001-inch polyethylene terephthalate film with a doctor blade set at 0.006 inch and dried overnight. The dried coating was exposed reflectographically (through the support) to a contacting resolution chart printed with blank ink on white paper, using a 500-watt tungsten filament lamp (General Electric reflector photoflood lamp ASA No. PH/RFL2) at a distance of 6 inches for 5 seconds. After exposure, the element was heated for a few seconds on a hot flat iron surface (170–180° C.) which resulted in the development of a black image in the exposed areas. The image was stabilized by thermal transfer of the unexposed areas to a paper receptor sheet. The transferred areas were converted to a black record by either heating the paper or exposing and heating.

EXAMPLE VIII

A photosensitive coating composition was prepared from the following ingredients:

	G.
Phenanthrenequinone	0.04
$\text{CF}_3\text{CHFCF}_2\text{SO}_3\text{Ag}$	0.10
Polyvinyl formal ¹	1.0
Acetone	11.0

¹ Formvar® 7/70 (Shawinigan Chemicals, Inc.), a resin with a molecular weight 21,000 (as a weight average), hydroxyl content of 5–7 (expressed as percent polyvinyl alcohol), acetate content of 40–50 (expressed as percent polyvinyl acetate) and having a specific gravity of 1.2.

The composition was coated and dried as in Example VII and exposed reflectographically to a line image using a 32-watt 60-cycle, 1-amp, white-light circular fluorescent tube through a translucent sheet for 10 sec. at 4 in. Then the element was passed over a roller having a temperature of 150–155° C. to cause the latent image to thermally develop to a brown-black image against a light yellow background. The yellow background color was later removed by an over-all exposure for two minutes at 12 inches distance to the photoflood lamp source described in Example VII. The color was due to unreacted phenanthrenequinone.

EXAMPLE IX

A photosensitive coating composition was prepared from the following ingredients:

Phenanthrenequinone—0.05 g.
 $\text{Ag}_2\text{B}_{12}\text{Cl}_{12}$ (prepared as described in assignee's copending application Cripps, U.S. Ser. No. 364,006, filed Apr. 30, 1964)—0.3 g.
Polyvinyl formal (as used in Example VIII)—1.0 g.
Acetone—10.0 ml.

The composition was coated and dried as in Example

VII and exposed through a photographic negative for 30 seconds at a distance of one inch using a phosphor-containing mercury vapor lamp emitting radiation chiefly from 3600 to 4200 angstroms (Aristo Grid Model B57).

The exposed element was thermally developed by contacting for 30 seconds with a flat iron surface at a temperature of 140–145° C., forming a dark brown image. In a similar composition, the single silver salt was replaced by a mixture of only 0.05 g. each of the above $\text{Ag}_2\text{B}_{12}\text{Cl}_{12}$ and the $\text{CF}_3\text{CHFCF}_2\text{SO}_3\text{Ag}$ of Example I. With a 5-second exposure and similar development conditions, there was obtained a black image.

EXAMPLE X

The following photosensitive coating mixture was coated and dried as in Example VII:

Phenanthrenequinone—0.04 g.
 $\text{CF}_3\text{CHFCF}_2\text{SO}_3\text{Ag}$ —0.09 g.
Polyvinyl formal (as used in Example VIII)—1.0 g.
Acetone—11.0 ml.

The dried film was given an imagewise exposure through a photographic negative for 10 seconds at a distance of 6 inches with the photoflood lamp of Example VII, overcoated with a thin layer of paraffin wax, and then thermally developed to a brown-black image by passing over a hot roll preheated to 150° C. A control element, without the wax overcoating, developed a similar dark brown image. When water was sprinkled on the surface of both the wax-overcoated developed image and the control image and both were subjected to the exposing light source for about 1 minute, a yellow background stain formed in nonimage areas of the control element but not on the wax overcoated element. Since water accelerated the aging process, it was thus shown that the wax overcoating was helpful in providing improved image stability. Similar improvement in stability was obtained when the overcoating was applied before image exposure.

EXAMPLE XI

The following photosensitive coating mixture was coated and dried as in Example VII:

1,4-Naphthoquinone—0.08 g.
Acetone—5.0 ml.
 $\text{CF}_3\text{CHFCF}_2\text{SO}_3\text{Ag}$ —0.3 g.
 $\text{Ag}_2\text{B}_{12}\text{Cl}_{12}$ —0.5 g.
 $(\text{CF}_3\text{CHFCF}_2\text{SO}_3)_2\text{Ba}$ ²—0.2 g.
Polyvinyl formal (as used in Example VIII)—0.7 g.

The resulting coating was placed in contact with a lead intensifying screen and exposed imagewise for one minute through a lead template to the radiation from a Philips X-ray Spectrograph (North American Philips Co.) operating at 50 kv./35 ma. A pale visible image was observed after the exposure and was intensified to a dark, brown-black image by thermal development for about 45 seconds, by contacting with a flat iron surface at a temperature of 145° C.

EXAMPLE XII

The following photosensitive coating mixture was coated and dried as in Example VII:

Benzoin phenyl thioether—0.2 g.
 $\text{CF}_3\text{CHFCF}_2\text{SO}_3\text{Ag}$ —0.1 g.
Polyvinyl formal (as used in Example VIII)—1.0 g.
Acetone—10.0 ml.

The coating was exposed for 2 minutes through a letter-text photographic transparency at a distance of 18 inches from a 45-amp. carbon arc lamp ("Nu Arc" lamp Model No. FT26M-2). Upon heating the exposed film at 140° C. for about 1 minute a grey image formed in the exposed areas.

² See footnote discussing preparation in Example I.

EXAMPLE XIII

The following photosensitive coating mixture was coated and dried as in Example VII:

	G.	
Methylene Blue Dye (CI Basic Blue 9) -----	.005	5
N-phenylglycine -----	.050	
CF ₃ CHF ₂ CF ₂ SO ₃ Ag -----	.15	
Polyvinyl formal as in Example I (15% by wt. solution 40/60 ethanol/toluene by weight) -----	7.5	10

This dried film which contained in initiating system comprising a photoreducible dye plus a reducing agent, was given an imagewise exposure through a photographic negative for 15 seconds at a distance of 12 inches with the photoflood lamp of Example VII. It was then thermally developed by contacting for 1 minute with a flat aluminum surface at a temperature of 120° C. A dark brown image was formed which was subsequently stabilized ("fixed") by washing in acetone to remove the dye. The stabilization step was also useful in lowering the background stain without appreciably affecting the image.

Similar results can be obtained by substituting for the Methylene Blue Dye, equivalent amounts of Safranin Blue B/N - phenylglycine, proflavine/N - phenylglycine and acriflavine/N-phenylglycine. Adequate images can be formed using the radiation source and heating conditions of Example XXIX.

EXAMPLE XIV

A photosensitive composition was prepared from the following materials and coated on 0.002-inch polyethylene terephthalate film with a doctor blade set at 0.006 inch.

	G.	
10% by weight aqueous solution of polyvinyl alcohol ¹ -----	10.0	35
Potassium phenanthrenequinone-3-sulfonate -----	0.05	
CF ₃ CHF ₂ CF ₂ SO ₃ Ag -----	0.10	
Diethyl phosphonoacetaldehyde diethyl acetal ----	0.30	

¹ A low viscosity grade, about 88% hydrolyzed.

The coating, which was dried in the dark for 3 hours, was given an imagewise exposure through a photographic negative for 10 seconds using the lamp described in Example IX. Thermal development at 140° C. for about 5 seconds afforded a light brown image in the exposed areas.

EXAMPLE XV

A photosensitive coating was prepared from the following solution and coated as described in Example XIV.

Phenanthrenequinone—0.05 g.	
Diethyl phosphonoacetaldehyde diethyl acetal—0.50 g.	
Polymethyl methacrylate ³ —1.0 g.	
CF ₃ CHF ₂ CF ₂ SO ₃ Ag—0.10 g.	
Acetone—7.0 ml.	

An imagewise exposure of 30 seconds through a photographic negative at a distance of one inch to the lamp of Example IX and thermal development for about 15 seconds on a roller heated to 140° C. afforded a grey-brown record in the exposed areas.

EXAMPLE XVI

A photosensitive composition was prepared from the following materials and coated as described in Example XIV:

Phenanthrenequinone—0.05 g.	
Benzoin methyl ether—1.10 g.	
CF ₃ CHF ₂ CF ₂ SO ₃ Ag—0.10 g.	
Polyvinyl formal of Example VIII—1.0 g.	
Acetone—12.0 g.	

³ A high molecular weight resin with an inherent viscosity of 1.20 for a solution containing 0.25 g. polymer in 50 ml. chloroform at 20° C.

The coating was exposed imagewise for 5 seconds at a distance of one inch to the lamp of Example IX and contact heated at 140° C. for 10 seconds. The coating was then placed against a sheet of paper and passed between two contacting rollers, one of which was heated to 140° C. The emerging sheets were quickly separated. A brown-black record of the exposed areas remained on the polyethylene terephthalate film and the yellow tinted unexposed areas transferred to the paper sheet. The transferred areas were darkened to a brown-black color by either heating the paper or exposing and heating.

EXAMPLE XVII

A photosensitive composition was prepared from the following materials and coated as described in Example XIV.

Phenanthrenequinone—0.05 g.	
CF ₃ CHF ₂ CF ₂ SO ₃ Ag—0.10 g.	
Cellulose acetate ⁴ —1.0 g.	
Diethyl phosphonoacetaldehyde diethyl acetal—0.30 g.	
Acetone—8.0 ml.	

A 30-second imagewise exposure at a distance of one inch to the lamp of Example IX and subsequent thermal development at 140° C. for about 10 seconds afforded a brown image in the exposed area. Thermal transfer of unexposed areas was accomplished by placing the imagewise exposed surface in contact with a piece of paper and passing a flat iron pre-heated to 145° C. over the polyethylene terephthalate support and immediately separating the two sheets. The transferred area was darkened by heating at 155° C. for about 1 minute.

EXAMPLE XVIII

A photosensitive composition was prepared from the following materials and coated as described in Example XIV.

Phenanthrenequinone—0.06 g.	
CF ₃ CHF ₂ CF ₂ SO ₃ Ag—0.12 g.	
Divinyl ether of 1,4-dimethylolcyclohexane—0.60 g.	
Polymethyl methacrylate described in Example XV—1.0 g.	
Acetone—8.0 ml.	

The coating was exposed for 5 minutes as described in Example IX and thermally developed by contacting for 10 seconds with a hot roller at a temperature of 135° C. A brown image was formed in the exposed areas.

EXAMPLE XIX

The following photosensitive coating mixture was coated and dried as in Example VII:

Phenanthrenequinone—0.04 g.	
CF ₃ COOAg—0.20 g.	
Polyvinyl formal (as used in Example VIII)—1.0 g.	
Acetone—11.0 ml.	

The dried film was given an imagewise exposure through a photographic negative for 60 seconds at a distance of 6 inches with the photoflood lamp of Example VII, and then thermally developed to produce an orange image by passing over a hot roll preheated to 145° C.

EXAMPLE XX

A photosensitive solution was prepared from the following ingredients:

Polyvinyl formal solution as described in Example I—15 g.	
Phenanthrenequinone—0.13 g.	
CF ₃ CHF ₂ CF ₂ SO ₃ Ag—0.3 g.	
(CF ₃ CHF ₂ CF ₂ SO ₃) ₂ Cu—0.1 g.	
Dioxane—4.0 ml.	

The mixture was coated and dried as described in Ex-

⁴ Characterized by having an acetyl content of 39.4% and an ASTM viscosity of 45.

ample VII. The coating was exposed in a 35 mm. camera, f-2 lens, for 15 seconds using two photolights, as described in Example I, to uniformly illuminate an 8½ x 11 inch white paper printed with black ink. After exposure the element was thermally developed as described in Example I. A black image corresponding to the white areas of the printed paper was formed.

EXAMPLE XXI

A photosensitive solution was prepared from

Phenanthrenequinone—0.06 g.
Cellulose acetate butyrate⁵—1.0 g.
CF₃CHFCF₂SO₃Ag—0.15 g.
Diethyl-(4 - hydroxy - 2,3,5,6 - tetrachlorophenyl)phosphate—0.50 g.
Triethyl phosphate—1.0 ml.
Acetone—11 ml.

and coated as described in Example XIV. The coating was exposed through a photographic negative for 15 seconds using the lamp described in Example IX. Thermal development at 140° C. produced an orange-brown image in the exposed areas. A very weak image formed when the halogenated phosphate was left out of the formulation. When both phosphate esters were omitted no imaging occurred.

EXAMPLE XXII

A photosensitive solution was prepared from

A mixture of polychlorinated biphenyl compounds
(as used in Example II) ----- 0.15
CF₃CHFCF₂SO₃Ag ----- 0.20
Divinyl ether of 1,4-dimethylolcyclohexane ----- 1.50
Polyvinyl formal as in Example VIII ----- 3.50

and coated as described in Example VII. A 15-second exposure was made at a distance of 6 inches to a 100-watt quartz-jacketed, water-cooled, high pressure mercury arc lamp cooled by an auxiliary air blower. Upon heating the exposed coating to 140° C., an orange-brown color formed in the exposed areas.

EXAMPLE XXIII

A photosensitive coating on 0.001-inch polyethylene terephthalate film was prepared from a solution containing

Phenanthrenequinone—0.025 g.
CF₃CHFCF₂SO₃Ag—0.025 g.
Polydioxolane⁶—0.50 g.

Tetrahydrofuran—4.00 cc.

The dry film was exposed through a photographic transparency for one minute at a distance of 12 inches from a 500-watt reflector type photoflood lamp as described in Example VII. The exposed surface was contacted with a sheet of white paper, briefly heated with a flatiron surface preheated to 75° C. and the two sheets were quickly separated. The exposed areas transferred to the paper receptor forming a grey-brown record, by repeating the thermal transfer process, using fresh sheets of paper, several copies were made. By exposing the residual unexposed areas and then thermally transferring this material to a new paper support a grey-brown copy of the original photographic transparency was made. Multiple copies were also made by repeating the procedure.

⁵ Characterized by a 20.5% by weight acetyl content and a 20% by weight butyryl content and having a viscosity range of 9.0–13.5 poises as determined by ASTM method D-1343-54T in the solution described as Formula A, ASTM method D-871-54T.

⁶ High molecular weight film forming polymer prepared by polymerizing dioxolane with boron trifluoride catalyst.

EXAMPLE XXIV

A photosensitive mixture was prepared from a solution of

Phenanthrenequinone—0.07 g.
Diethyl phosphonoacetaldehyde diethylacetal—0.20 g.
Polyvinyl formal as in Example VIII—1.0 g.
Lithium bromide—0.087 g.
Acetone—9.0 ml. by adding
CF₃CHFCF₂SO₃Ag—0.34 g.
Dissolved in acetone—2.0 ml.

and stirring for two minutes. The mixture was coated as in Example XIV forming a dry hazy coating containing a fine dispersion of silver bromide. The coating was exposed through a photographic negative for two seconds using the lamp described in Example IX. Thermal development at 165° C. produced a black image in the exposed area. Similar results were obtained by exposing for 10 seconds at a distance of 2 inches from a 100-watt tungsten lamp and developing at 165° C.

EXAMPLE XXV

A photosensitive coating was prepared as in Example XXIV using 0.15 g. sodium iodide in place of the lithium bromide. The hazy dry coating was exposed for one second using the lamp described in Example IX and developed at 175° C. to form a black image. A pale grey image was visible after exposure and before heating. Similar results were obtained by exposing for 5 seconds using the tungsten lamp of Example XXIV and developing at 175° C. A 4-minute exposure to the tungsten lamp produced a strong red image which turned black during thermal development.

EXAMPLE XXVI

To a photosensitive solution prepared from

Phenanthrenequinone—0.10 g.
CF₃CHFCF₂SO₃Ag—0.10 g.
Polyvinyl formal as in Example VIII—1.0 g.
Acetone—10.0 ml. was added
Finely divided silica having particle sizes of 10–20 millimicrons⁷—0.3 g.

A similar solution was prepared from which the silica was omitted. Coatings were prepared as described in Example XIV and exposed for 10 seconds through a √2 photographic step wedge using the lamp described in Example IX. The two exposed samples were simultaneously developed by contacting the exposed surface with a sheet of paper and heating the supports with a flatiron preheated to 135° C. for one minute. Twelve steps were readable in the silica-containing coating whereas only nine steps developed in the control coating. Longer heating time was required to develop a twelve-step image in the control and this longer heating time caused image spread and thermal fog.

EXAMPLE XXVIII

A mixture of

	G.
Phenanthrenequinone -----	0.1
CF ₃ CHFCF ₂ SO ₃ Ag -----	0.3
Polyamide (nylon) resin having a Brookfield viscosity of 110 c.p. at 25° C. in 80% aqueous ethanol -----	1.6
Distilled water -----	3.2
Absolute alcohol -----	10.2

was coated on 0.002-inch polyethylene terephthalate film with a 0.006-inch doctor knife. The dried coating was exposed 30 seconds at 12-inch distance to actinic radiation using a Sylvania Sun Gun II, model SG-55, tungsten

⁷ The colloidal silica was obtained from an aqueous dispersion of 4 g. silica in 100 ml. water having a pH of 7; refractive index of 1.475 (Dow-Corning).

filament lamp type DWY. Heating with a platen at 160° C. for 30 seconds produced a yellow negative image.

EXAMPLE XXIX

A mixture of

Phenanthrenequinone	G. 0.1
CF ₃ CHFCF ₂ SO ₃ Ag	0.3
Poly(methyl vinyl ether/maleic anhydride) of specific viscosity 2.6–3.5 (high molecular weight grade)	1.7
Acetone	13.3

was coated on a 0.002-inch polyethylene terephthalate film with a 0.006-inch doctor knife. The dried coating was exposed 30 seconds at a distance of 12 inches from the lamp of Example XXVIII. Heating with a platen at 160° C. for 10 seconds produced a gray-brown negative image with some background stain.

EXAMPLE XXX

A mixture of

Phenanthrenequinone	G. 0.1
CF ₃ CHFCF ₂ SO ₃ Ag	0.2
Gelatin (low pH blend)	1.4
Distilled water	13.6

was coated on 0.002-inch polyethylene terephthalate film with a 0.006-inch doctor knife. The dried coating was exposed for 30 seconds at a distance of 12 inches from the lamp of Example XXVIII. Heating with a platen at 160° C. for 30 seconds produced a yellow negative image.

EXAMPLE XXXI

A mixture of

Phenanthrenequinone	G. 0.1
CF ₃ CHFCF ₂ SO ₃ Ag	0.2
Poly(methyl methacrylate, 35 mole percent—acrylonitrile, 40 mole percent—acrylated glycidyl acrylate, 25 mole percent) prepared according to the procedure of assignee's copending application of Schoenthaler, Ser. No. 451,300 filed April 27, 1965	1.7
Acetone	13.3

was coated on 0.002-inch polyethylene terephthalate film with a 0.006-inch doctor knife. The dried coating was exposed 30 seconds at a 12-inch distance to the lamp of Example XXVIII. Heating with a platen at 160° C. for 5 seconds produced a yellow-gray negative image.

EXAMPLE XXXII

A photosensitive coating was prepared from

Phenanthrenequinone—0.08 g.
Polyethylene glycol; avg. mol. wt. 400—0.20 g.
Pinacol hydrate—0.2 g.
CF ₃ CHFCF ₂ SO ₃ Ag—0.1 g.
Polymethyl methacrylate of Example XV—0.96 g.
Acetone—10 ml.

which was coated on 0.002-inch polyethylene terephthalate film using a 0.006 doctor knife. After drying, the coating was exposed for 10 seconds using the lamp of Example IX and was heated at 150° C. for a few seconds. Yellow images were formed in the exposed areas.

Similar colored images were obtained upon adding the plasticizer, dibutyl phthalate, to the above composition.

EXAMPLE XXXIII

A mixture of

Phenanthrenequinone	G. 0.1
CF ₃ CHFCF ₂ SO ₃ Ag	0.2

Poly(vinyl chloride/vinyl acetate) 90/10 mole percent, inherent viscosity 0.80 (A.S.T.M. procedure) specific gravity 1.36	1.7
Acetone	13.3

was coated on 0.002-inch polyethylene terephthalate film with a doctor knife. The dried coating was exposed for 30 seconds at a distance of 12 inches from the lamp of Example XXVIII. Heating with a platen at 160° C. for 10 seconds produced a red-brown negative image.

EXAMPLE XXXIV

A photosensitive solution was prepared from

Phenanthrenequinone—0.08 g.
CF ₃ CHFCF ₂ SO ₃ Ag—0.1 g.
Cetyl vinyl ether—0.6 g.
Pinacol hydrate—0.2 g.
Polymethyl methacrylate of Example XV—0.96 g.
Acetone—10 ml.

and coated on 0.002-inch polyethylene terephthalate film using a 0.006-inch doctor knife. After drying for a one-half hour, the coating was exposed through a photographic transparency for 5 seconds using the lamp of Example IX and was heated at 160° C. for a few seconds. A brown image formed in the exposed areas.

EXAMPLE XXXV

A photosensitive coating was prepared from

Phenanthrenequinone—0.08 g.
CF ₃ CHFCF ₂ SO ₃ Ag—0.2 g.
Water-soluble starch—0.8 g.
Pinacol hydrate—0.2 g.
Acetone—10 ml.

The dry film was exposed for 20 seconds as described in Example IX and when heated at 160° C. formed brown-black images in the exposed areas.

When the starch in the above composition was replaced by 0.8 g. sucrose, a 10-second exposure and 130° C. thermal development produced brown-black images in the exposed areas.

When the starch was replaced by 0.8 g. D-ribose, a 10-second exposure and 160° C. thermal development produced brown-black images in exposed areas. Similar results were obtained in replacing starch by 0.8 g. sorbitol.

EXAMPLE XXXVI

A photosensitive coating was prepared from

Phenanthrenequinone—0.08 g.
CF ₃ CHFCF ₂ SO ₃ Ag—0.2 g.
Polyethylene glycol of mol. wt. 400—0.2 g.
Sucrose octaacetate—0.5 g.
Pinacol hydrate—0.2 g.
Polymethyl methacrylate of Example XV—0.96 g.
Acetone—10 ml.

A 10-second exposure using the radiation source of Example IX and heating at 150° C. produced brown-black images in the exposed areas.

EXAMPLE XXXVII

Films were made from solutions containing

Ketone photoinitiator, where the ketone is benzophenone, p-hydroxybenzophenone, p-aminobenzophenone, acetophenone or p-hydroxyacetophenone	G. 0.10
Silver fluorosulfonate CF ₃ CHFCF ₂ SO ₃ Ag	0.20
15% (by weight) in acetone of the polyvinyl formal of Example VIII	7.5

by coating the solutions onto 0.002-inch polyethylene terephthalate film using a 0.006 inch doctor knife. The dried films were exposed through a photographic negative to actinic radiation using a Nu-Arc carbon arc at full intensity or 8 flashes (1/500 sec. duration each), a Hico xenon

photoflash lamp, model K at one-inch or a Blue-ray printer lamp, model 159. Thermal development at 160° C. for 5 seconds produced a black image in the exposed areas. Addition of 0.5 gram pinacol hydrate aided the image formation.

EXAMPLE XXXVIII

A photosensitive coating was prepared from

Phenanthrenequinone—0.06 g.
 $\text{CF}_3\text{CHF}_2\text{SO}_3\text{Ag}$ —0.1 g.
 Pinacol hydrate—0.5 g.
 Triethylene glycol diacetate—0.4 g.
 Acetic acid (glacial)—1 ml.
 Polymethyl methacrylate as described in Example XV—0.96 g.
 Acetone—10 ml.

The slightly tacky coating was exposed for 10 seconds using the lamp described in Example IX. A bright green image was produced in the exposed areas of the film which changed to a yellow color when heated at 100° C.

When the film was allowed to dry to a non-tacky stage, yellow images were obtained after a 10-second exposure and red ones after a 60-second exposure. When the non-tacky film was preconditioned in an acetic atmosphere, green images were obtained during exposure.

When acetic acid was omitted from the above formulation and the dry coating was exposed for 20 seconds and thermally developed at 100° C., yellow images were formed. By briefly treating the exposed surface with a cotton swab saturated with acetic acid, the yellow images became red or black depending on the duration of the treatment. Similar color changes took place with ethyl acetate, acetone, methylene chloride or ethanolic acetic acid.

EXAMPLE XXXIX

A photosensitive coating supported on a thin glass plate was prepared from

1,4-naphthaquinone—0.08 g.
 Half-ester of succinic anhydride and polyethylene glycol monomethyl ether of molecular weight 750—0.3 g.
 $\text{CH}_3\text{CHF}_2\text{SO}_3\text{Ag}$ —0.1 g.
 Polymethyl methacrylate of Example XV—1.0 g.
 Acetone—10 ml.

and was exposed for $\frac{1}{500}$ second using Model K HICO-LITE electronic flash having an output of 200 watt seconds. After exposure it was briefly soaked in a 1:1 by volume ethanol-water solution and heated at about 275–300° C. during which time the methacrylate in the unexposed areas was removed via depolymerization and volatilization and a gray image remained in the exposed areas.

EXAMPLE XL

A photosensitive solution prepared from

Phenanthrenequinone—0.08 g.
 $\text{CF}_3\text{CHF}_2\text{SO}_3\text{Ag}$ —0.15 g.
 Diethylphosphonoacetaldehyde diethylacetal—9 ml.

was poured onto a thin sheet of asbestos paper and allowed to soak in. An imagewise exposure of 20 seconds using the lamp described in Example IX produced a yellow-brown image which darkened when heated briefly at 160° C.

EXAMPLE XLI

A photosensitive solution prepared from

Phenanthrenequinone—0.08 g.
 $\text{CF}_3\text{CHF}_2\text{SO}_3\text{Ag}$ —0.15 g.
 Diethylphosphonoacetaldehyde diethylacetal—0.3 g.
 Cellulose acetate N,N-diethylaminoacetate—1.5 g.
 Acetone—10 ml.

The coating was prepared in the usual way and after drying for one-half hour the film was exposed for 20

seconds using the lamp described in Example IX. An orange image was formed in the exposed areas which darkened when briefly heated at 160° C. Continued heating at 175–180° C. caused the orange image area to become yellow and the unexposed areas to turn red.

5 In its simplest form, the image-forming layer in the elements of this invention need consist only of (a) a silver salt of a strong acid, (b) a photosensitizer, (c) a hydrogen abstractable material, and (d) a carrier, preferably a film-forming organic polymer binder. Although a hydrogen abstractable material or hydrogen donor compound (c) is an essential component, while an acid-sensitive organic material (e) and water, or a water-yielding material or compound (f) are components present in preferred compositions, the functions of these three components may be supplied by the polymer binder (d) alone. Therefore, in defining the image-forming layer of the simplest form of the invention, for 100 parts by weight of polymer binder (d) there may be present in the image-forming layer in an amount from 2 to 200 parts, preferably from 4 to 50, parts by weight, of silver salt (a). The concentration of photosensitizer (b) is related to that of the silver salt so that for each 100 parts of (a) there may be from 10 to 300 parts, preferably from 20 to 100 parts, of the photosensitizer (b).

10 In the broadest concept of this invention, component (d) may be a carrier which includes polymer binders as well as sheets of porous paper, asbestos fiber, fiber glass, etc. Since the film forming organic polymer binder is optional, its lower limit of concentration can be zero while the upper limit can be about 95% of the total weight of the image-forming layer (exclusive of solvents). A solvent is normally present, but is usually removed during drying. The amount of solvent in the coating composition depends on the desired coating thickness which may vary from thin coatings, e.g., 0.00001 to 0.001 inch for office copy elements, to thicker coatings, e.g., 0.003 to 0.25 inch for relief printing plates as disclosed in U.S. Pat. 2,760,863.

15 Constituent (c) should be 5 times the weight of constituent (b). However, a manifold excess of constituent (c) can be present.

20 The layer preferably contains water or a water-yielding material (f), although the water source may be the polymer binder, or even air if processing is carried out in an atmosphere of high relative humidity.

25 A preferred class of photosensitizers for component (b), the photoreducible materials which are activatable by actinic light and thermally inactive at and below 185° C., includes the substituted or unsubstituted polynuclear quinones which are compounds having two intracyclic carbonyl groups attached to intracyclic carbon atoms in a conjugated carbocyclic ring system. Suitable such materials include 9,10 - anthraquinone, 1-chloroanthraquinone, 2 - chloroanthraquinone, 2 - methylanthraquinone, 2 - ethylanthraquinone, 2 - tert-butylanthraquinone, octamethylanthraquinone, 1,4 - naphthoquinone, 9,10 - phenanthrenequinone, 1,2 - benzantraquinone, 2,3 - benzantraquinone, 2 - methyl - 1,4 - naphthoquinone, 2,3 - dichloronaphthoquinone, 1,4 - dimethylanthraquinone, 2,3-diphenylanthraquinone, sodium salt of anthraquinone alpha-sulfonic acid, 3 - chloro - 2 - methylanthraquinone, retenequinone, thymoquinone, 7,8,9,10 - tetrahydronaphthacenequinone, and 1,2,3,4 - tetrahydrobenz(a)anthracene - 7,12 - dione. Other photosensitizers which are also useful, even though some may be thermally active at temperatures as low as 85° C., are described in Plambeck U.S. Pat. 2,760,863 and include vicinal ketaldonyl compounds, such as diacetyl, benzil, etc., alphaketaldonyl alcohols, acyloin ethers, e.g., benzoin methyl and ethyl ethers, etc.; alpha-hydrocarbon substituted aromatic acyl-30 oins, including alpha-methylbenzoin, alpha-allylbenzoin, and alpha-phenylbenzoin; and photoreducible dyes including those described in Example XIII.

35 In assignee's copending application of Cripps, Ser. No. 364,006, filed Apr. 30, 1964, U.S.P. 3,347,676, Oct. 17,

1967, there are listed a number of silver salts of strong acids which may be used satisfactorily as component (a). These include silver salts of highly fluorinated alkanesulfonic acids, in particular perfluoroalkanesulfonic acids or beta-hydroperfluoroalkanesulfonic acids and silver salts of decahydrodecaboric acids, i.e., salts of dihydrogen substituted decahydrodecaborates (2-), or of substituted dodecahydrododecaboric acids, i.e., salts of dihydrogen substituted dodecahydrodecaborates (2-).

When the water-yielding compound (f) is present, useful compounds include alkanols of 4-8 carbon atoms, e.g., t-butyl, n-pentyl, t-amyl and n-octyl alcohol; especially dihydroxyalcohols, e.g., pinacols (and their hydrates) containing tertiary alkyl groups, e.g., t-butyl and t-amyl, and benzpinacol.

The polymer binder (d) can be an organic polymer of molecular weight greater than 10,000, capable of forming hard, coherent, thin films and inert, i.e., substantially free from amounts of labile, covalent halogen. Suitable polymers include alkyl esters of polyacrylic and polymethacrylic acid, e.g., polymethyl methacrylate, polyethyl methacrylate and the corresponding acrylates; cellulose carboxylic acid esters and ethers, e.g., cellulose acetate, cellulose propionate, cellulose acetate butyrate, methyl, ethyl and benzyl cellulose; polyvinyl alcohol and its partial esters and acetals. Thermoplastic polymeric binders are preferred so that the element may be useful in the process of thermal image transfer. However, when thermal transfer is not required, it is also possible to use non-thermoplastic polymeric binders, such as polyvinyl alcohol. As shown in one of the examples, a useful element may be made in the complete absence of a binder, particularly if the light-sensitive system is applied to a porous support, such as paper, in which case the support itself may be considered as a binder.

Suitable acid-sensitive organic materials that have binder properties, in addition to the specific materials listed above, include polydioxolanes and any of the polyoxymethylene compounds that are disclosed in U.S. Patent, Alsop et al. 2,993,025.

A number of other materials may be present in the image-forming system such as coating aids, e.g., polyethylene oxides, viscosity modifiers e.g., dibutyl phthalate, silica or cellulosic fillers, etc.; colorants, e.g., pigments or dyes which transmit effectively in the actinic region of the spectrum, etc.

The present invention offers the advantage of providing an image-forming system which combines simplicity of use and apparatus with quality results. Image quality which is customarily obtained via elaborate processing (wet processing) is herein obtained by the simple, dry steps of merely exposing and heat developing. The image has very fine grain, high resolution, high contrast and a wide range of density. A simple fixing step is optional although the developed images are reasonably stable as long as they are not subjected to excessive heat. The system offers flexibility in that the developed image may be used as first developed, it may be transferred to a separate receptor support by thermal transfer, or it may be given a washout treatment to physically remove all or part of the non-image areas. By thermal transfer it is possible to obtain both positive and negative images. This thermal development system has potentially high photo-speed and can produce images with transmission optical densities greater than 4.0 on a fog-free background.

Because the developed image has very fine grain and very high resolution, it is particularly useful in microfilm reproduction. Light sensitivity of the elements of this invention is more than adequate for any type of copying operation, e.g., printing by contact or enlargement. Even camera speed has been demonstrated with exposures of about five seconds at *f*4 with proper illumination and the system has potential capabilities of considerably more speed.

The compositions described above can be coated or

applied to various kinds of supports, e.g., plates, films, foils, webs and sheets, including the specific supports and using the coating, spreading and calendering procedures described in each of the patents listed above. Similar layers can be made with or without the use of the solvents described above and/or other solvents. Plasticizers can be used which include dibutyl phthalate and tricresyl phosphate. The versatile character of the compositions is a decided advantage of the invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An image-yielding element comprising a support bearing an image-forming layer comprising

(a) a silver salt of a perfluoroalkanesulfonic acid or a beta-hydroperfluoroalkanesulfonic acid or a decahydrodecaboric acid, said acid having a stable anion and a pKa no greater than 2,

(b) a photosensitizer capable, upon absorption of actinic radiation, of decomposing said silver salt to liberate a strong acid taken from the group consisting of photoreducible quinones, alpha-diketones, benzpinacolone, polychlorinated biphenyl, bromonaphthalene and photoreducible dyes,

(c) a hydrogen abstractable material or compound which is a hydrogen donor for said photosensitizer during its absorption of actinic radiation selected from the class consisting of an alcohol, an acetal, diethylene glycol and its monomethyl ether or diacetic acid ester, a polyethylene glycol of molecular weight 400-6000 and tetraethyl malondialdehyde acetal, and

(d) a film forming organic polymer binding agent free from substantial amounts of labile covalent halogen; said layer being characterized in that for every 100 parts of (d) there are 2 to 200 parts of (a) and for every 100 parts of (a) there are 10 to 300 parts of (b), and constituent (c) is present in an amount 5 times the weight of (b) but can be present in an amount 0 times the weight of (b) when (d) is the hydrogen donor for (b), the parts being by weight.

2. An element according to claim 1, wherein component (b) is a substituted or unsubstituted polynuclear quinone having two intra-cyclic carbonyl groups attached to intra-cyclic carbon atoms in a conjugation ring system.

3. An image-yielding element comprising a support bearing an image-forming layer comprising

(a) a silver salt of a perfluoroalkanesulfonic acid or a beta-hydroperfluoroalkanesulfonic acid or a decahydrodecaboric acid, said acid having a stable anion and a pKa no greater than 2,

(b) a photosensitizer capable, upon absorption of actinic radiation, or decomposing said silver salt to liberate a strong acid taken from the group consisting of photoreducible quinones, alpha-diketones, benzpinacolone, polychlorinated biphenyl, bromonaphthalene and photoreducible dyes,

(c) a hydrogen abstractable material or compound which is a hydrogen donor for said photosensitizer during its absorption of actinic radiation selected from the class consisting of an alcohol, an acetal, diethylene glycol and its monomethyl ether or diacetic acid ester, a polyethylene glycol of molecular weight 400-6000 and tetraethyl malondialdehyde acetal, and

(d) a film-forming organic polymer binder free from substantial amounts of labile covalent halogen and at least one of the following:

(e) an acid-sensitive aldehyde precursor or polymeric acetal which produces a color change in the presence of a strong acid having a pKa no greater than 2.0, said color change being sufficient to form a visible image, and

(f) is water or a water-yielding compound selected

17

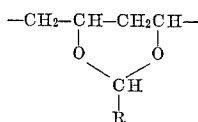
from the group consisting of alkanols of 4-8 carbon atoms, pinacols and their hydrates containing tertiary alkyl groups and benzpinacol,

said layer being characterized in that for every 100 parts of (d) there are 2 to 200 parts of (a) and for every 100 parts of (a) there are 10 to 300 parts of (b), and constituent (c) is present in an amount 5 times the weight of (b), but can be present in an amount 0 times the weight of (b) when (d) is the hydrogen donor for (b), the parts being by weight.

4. An element according to claim 3, wherein component (b) is a substituted or unsubstituted polynuclear quinone having two intra-cyclic carbonyl groups attached to intra-cyclic carbon atoms in a conjugation carbocyclic ring system.

5. An element according to claim 3, wherein component (c) is an alkanol of 4-8 carbon atoms.

6. An element according to claim 3, wherein component (e) is a polymeric acetal which contains intralinear units of the structure



where R is H or $\text{CH}_3\text{CH}_2\text{CH}_2\text{---}$.

18

7. A process which comprises

(1) exposing, imagewise, to actinic radiation predominating in wavelengths in the ultraviolet and visible regions of the spectrum an image-yielding element having an image-forming layer as defined in claim 1, and

(2) uniformly heating the exposed stratum to a temperature between 60° C. and 200° C. to effect dry development of an image.

8. A process which comprises

(1) exposing, imagewise, to actinic radiation predominating in wavelengths in the ultraviolet and visible regions of the spectrum an image-yielding element having an image-forming layer as defined in claim 3, and

(2) uniformly heating the exposed stratum to a temperature between 60° C. and 200° C. to effect dry development of an image.

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