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PHOTOTHERMOGRAPHIC ELEMENTS AND METHOD OF USING SAME

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Fig. 1

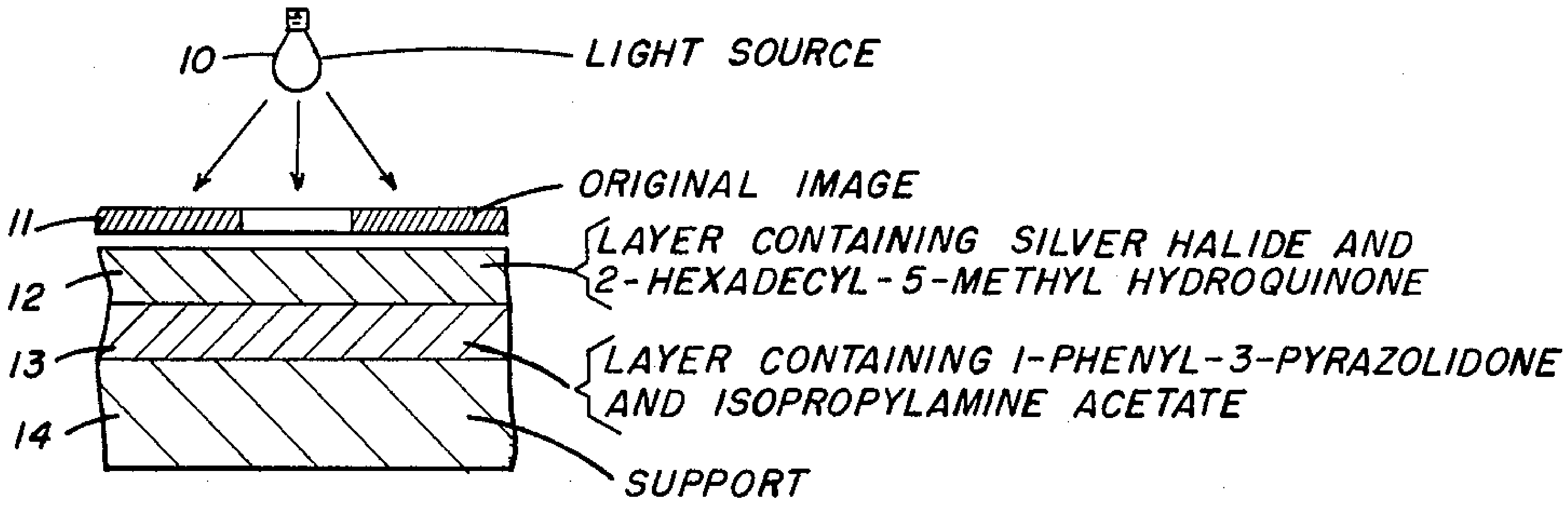


Fig. 2

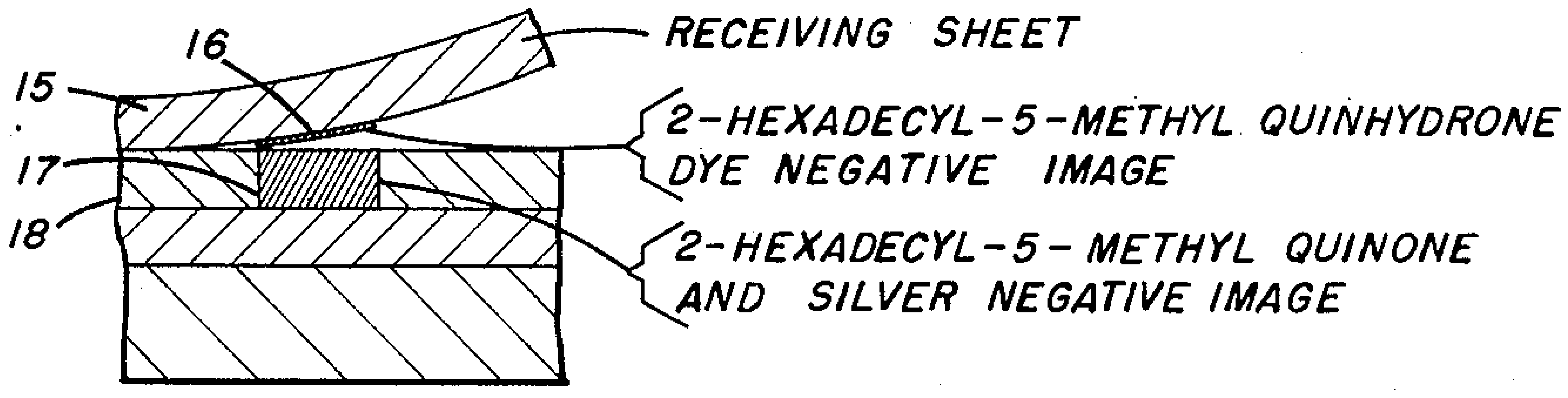
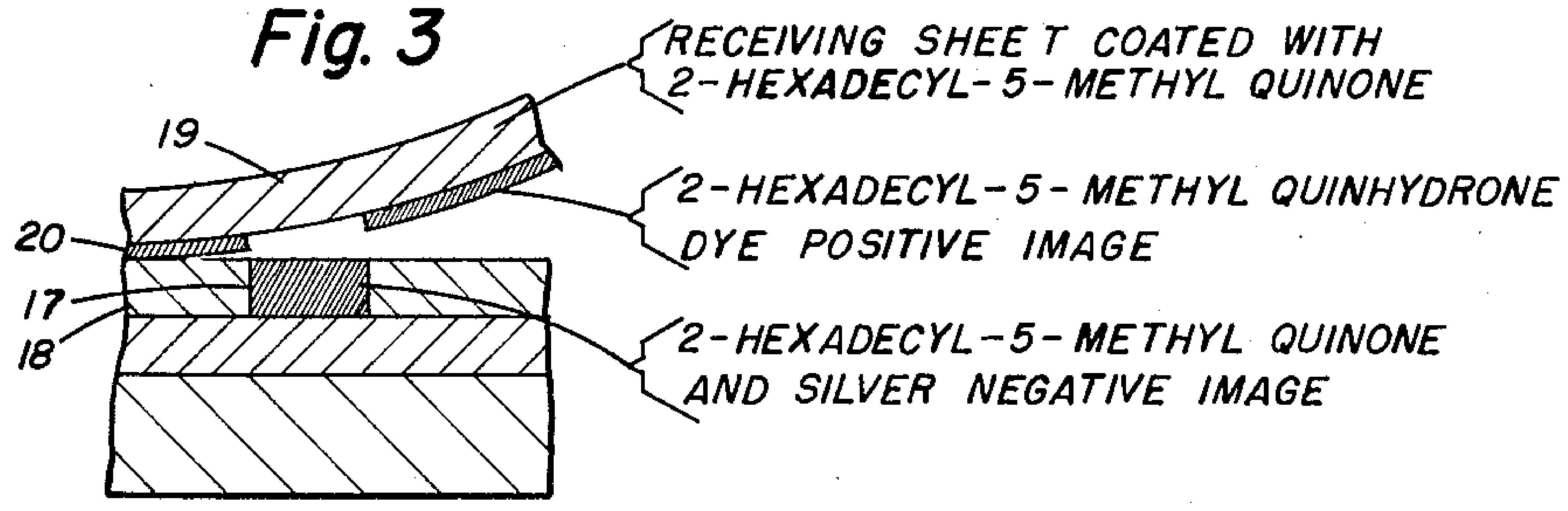


Fig. 3



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PHOTOTHERMOGRAPHIC ELEMENTS AND METHOD OF USING SAME

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9 Claims. (Cl. 96—29)

This invention relates to novel light-sensitive elements and more particularly to novel light-sensitive photothermographic elements and their heat processing to produce colored images by cross-oxidation reactions.

Photothermographic elements are known in the art. These materials are designed for exposure to a light image which creates an invisible latent image that is subsequently made visible by the action of heat. British 790,811, published February 19, 1958, for example, describes such a material which contains a light-sensitive silver halide emulsion and a developer. After exposure, this material is heat developed and the developing agent which remains unused in the unexposed areas is transferred to a receiving sheet containing a diazo compound with the production of a corresponding dye image.

The formation of colored quinhydrone images by heat has been proposed for preparing a thermographic paper. However, heretofore, it has not been possible to prepare such a compound by thermographic development of a silver halide emulsion layer.

It is an object of our invention to provide a novel, light-sensitive photothermographic element for producing colored images.

Another object of our invention is to provide a new class of light-sensitive photothermographic elements for producing colored images by cross-oxidation reactions.

Another object is to provide photothermographic elements which are processed with a rapid, substantially dry process to produce copies of good quality.

Another object is to provide photothermographic elements that are valuable for copying originals by contact printing with transmitted light or by reflex printing, or by projection printing.

Another object is to provide novel photothermographic elements which have high photographic speeds which makes them valuable for use in cameras of the Photostat copier type.

Still another object is to provide a process for processing our novel photothermographic material.

Still further objects will become apparent from the following specification and claims.

These and other objects are accomplished by using the photothermographic element of our invention.

Our light-sensitive photothermographic element consists of (1) a support coated with (2) a silver halide developing layer in a hydrophilic binder and coated over this (3) a second hydrophilic layer comprising a dispersion of light-sensitive silver halide and a dispersion of an organic composition which changes color upon cross-oxidation, said composition being dissolved in a substantially water-insoluble alkali-permeable organic solvent. In certain instances, the constituents of layers (2) and (3) are combined in a single layer.

In one preferred embodiment of our invention, the photothermographic element consists of (1) a support coated with (2) a developer layer comprising a hydrophilic binder, a substituted cyclic nontanning silver halide developing agent and an alkaline salt, said layer coated with (3) a second hydrophilic layer comprising a binder

having dispersed therein light-sensitive silver halide and a substantially water-insoluble 2-alkyl-5-alkyl substituted hydroquinone dissolved in a substantially water-insoluble alkali-permeable organic solvent. Alternatively, this element may contain in addition to the dispersion of 2-alkyl-5-alkyl substituted hydroquinone in the second hydrophilic layer, a second dispersion comprising a solution of a substantially water-insoluble 2-alkyl-5-alkyl substituted quinone in a substantially water-insoluble alkali-permeable organic solvent or may contain instead of the two dispersions only the dispersion of 2-alkyl-5-alkyl substituted quinone dissolved in the organic solvent.

In another embodiment of our invention, the element consists of (1) the support, (2) the developer layer already described and (3) a second hydrophilic layer comprising a binder having dispersed therein light-sensitive silver halide and a solution of a substantially water-insoluble dye base of the alkoxynaphthol series dissolved in a substantially water-insoluble alkali-permeable organic solvent.

In another preferred embodiment of our invention the element consists of (1) the support and (2) developer layer already described and (3) a second hydrophilic layer comprising a binder having dispersed therein light-sensitive silver halide and a solution of a substantially water-insoluble leuco dye dissolved in a substantially water-insoluble alkali-permeable organic solvent.

In still another preferred embodiment of our invention, the element consists of (1) the support and (2) developer layer already described and (3) a second hydrophilic layer comprising a binder having dispersed therein light-sensitive silver halide and a solution of a substantially water-insoluble p-phenylenediamine and a substantially water-insoluble color-forming coupler in a substantially water-insoluble alkali-permeable organic solvent.

Our photothermographic elements are exposed to a light image by contact printing either by transmission or by reflex, projection printing or with a camera such as is used in a Photostat copier, developed by treating the exposed element with steam to bring the material to a temperature in the range of from 70 to 100° C., then the hydrophilic layer of the hot element is immediately contacted with a paper receiving sheet to produce the copy bearing a dye image. One additional copy is made by contacting the hot element with a fresh paper receiving sheet. The steam heat development may be accomplished in any convenient manner such as passing the element for about 15 seconds close to a supply of steam such as a steam laundry iron; or alternatively, the element can be uniformly moistened with water and then exposed to a dry heat to raise the temperature of the element to the processing temperature. A particularly advantageous method involves passing the exposed element between a pair of driven rollers which moisten the element with water at room temperature, convey the moist element through a heat tunnel made by two heated blocks of metal to another set of driven rollers which remove the hot element from the tunnel and contact its hydrophilic layer with a paper receiving sheet. The copy is then stripped from the hot element.

The optimum heating time will depend upon the temperature of the steam, heating tunnel or other device used and can be readily determined.

The formation of the colored image corresponding to the light exposed latent image during the thermographic processing of each of the described types of elements involves the development of a silver image in the second hydrophilic layer with the imagewise formation of oxidized and unoxidized silver halide developer which then undergoes a cross-oxidation reaction with the substantially water-insoluble color-forming organic composition dissolved in the dispersed particles of substantially water-insoluble alkali-permeable organic solvent. The details of the cross-oxidation reaction depend upon the materials used in the color-forming organic composition and determine whether a negative or positive image is obtained of the original. Usually, the colored image formed by the cross-oxidation reaction is transferred from the hot developed element to a paper receiving sheet which may or may not contain another material that enters into the color-forming reaction. This will also determine whether the image is a negative or positive of the original.

The transfer step in our process not only permits making two or sometimes several copies but has the very important advantage of producing copies that are substantially free of the various chemicals that are in the element. Thus the copies produced have optimum stability.

By cross-oxidation we mean the reaction mechanism by which either (1) the silver halide developing agent oxidized by silver halide development in turn oxidizes the reduced form of a color-forming composition used in the photothermographic element, or (2) the reaction in which unused silver halide developing agent reduces the oxidized form of a color-forming composition used in the element.

The elements which have as the color-forming organic compositions a 2-alkyl-5-alkyl substituted hydroquinone, a dye base, a leuco dye, or a combination of a color-forming coupler and a substantially water-insoluble substituted p-phenylenediamine are believed to involve a cross-oxidation reaction in which the oxidized silver halide developing agent, formed by silver image development, oxidizes some of the color-forming organic composition to produce a negative image of the original image.

In an element containing a substituted hydroquinone, the oxidized silver halide developing agent oxidizes some of the substituted hydroquinone to the corresponding quinone which while still hot is transferred with unoxidized hydroquinone to a paper receiving sheet where the corresponding negative quinhydrone dye image is formed when the paper cools. Alternatively, a positive quinhydrone image of the original is produced from this element when the receiving sheet used contains a coating of the appropriate substituted quinone.

In a product containing a dye of the alkoxynaphthol series, the oxidized developer formed in the exposed areas oxidizes the dye base by a cross-oxidation reaction to produce a dye negative image of the original which is then transferred while hot to a plain paper receiving sheet.

In an element containing a leuco dye, the imagewise oxidized silver halide developing agent cross-oxidizes the leuco dye to produce a negative dye image of the original which is then transferred while hot to a plain paper receiving sheet.

In an element containing a color-forming coupler and a substantially water-insoluble substituted p-phenylenediamine developing agent, the imagewise oxidized silver halide developing agent cross-oxidizes the p-phenylenediamine to its oxidized form which reacts with the coupler to produce a negative dye image of the original which is then transferred while hot to a plain paper receiving sheet.

The reversibility of the reaction system

substituted hydroquinone $\rightleftharpoons$ substituted quinone

in the water-insoluble alkali-permeable organic solvents is used in another cross-oxidation reaction to form a direct positive without using a receiving sheet coated with the appropriate quinone as described above. This is accomplished by substituting a 2-alkyl-5-alkyl substituted quinone for the substituted hydroquinone as the color-forming composition in the element of this type described previously. The immediate element uses preferably a 1-phenyl-3-pyrazolidone as a silver halide developing agent. The unused unoxidized 1-phenyl-3-pyrazolidone left in areas of unexposed silver halide upon thermographic processing reduce some of the substituted quinone to the corresponding hydroquinone which while still hot is transferred to the paper receiving sheet where a positive quinhydrone dye image is formed of the original. No dye is formed corresponding to the exposed areas of the silver halide since none of the quinone in those areas is reduced to the hydroquinone.

In another element designed for the direct production of positive dye images utilizing preferably a p-methylaminophenol sulfate as the silver halide developing agent, the second hydrophilic layer comprises a hydrophilic binder having dispersed therein silver halide, a 2-alkyl-5-alkyl substituted hydroquinone dissolved in a substantially water-insoluble alkali-permeable organic solvent and a 2-alkyl-5-alkyl substituted quinone dissolved in substantially water-insoluble alkali-permeable organic solvent. During thermographic processing, the oxidized form of the silver halide developing agent formed in areas of silver image development cross-oxidizes all the substituted hydroquinone to its quinone so upon transfer, a positive dye image of the original is formed on the paper receiving sheet.

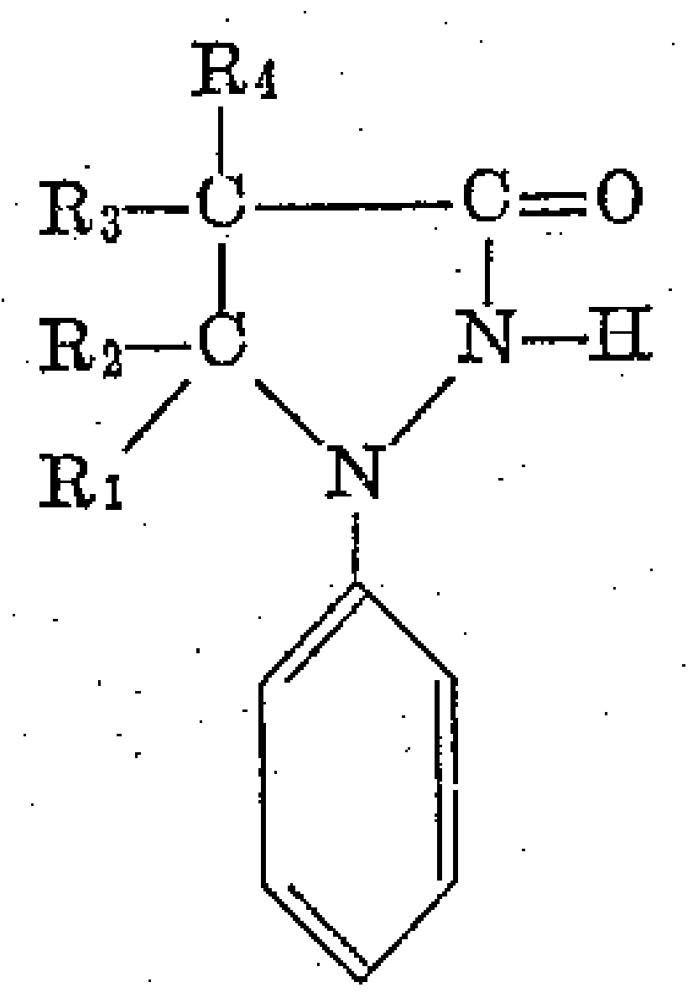
The following description will further illustrate our photothermographic elements.

The support for our elements can be any of the support materials used in photography, such as paper, sheet metal, glass, plastic sheeting made out of materials such as polyethylene terephthalate, the polycarbonates, etc.

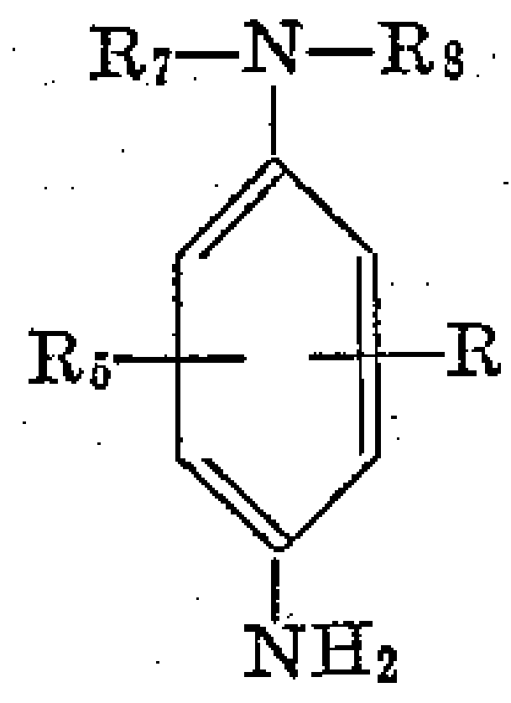
The hydrophilic binder used in the hydrophilic colloid layers to contain the various chemicals in the photothermographic element can be any gelatin such as is used in photographic materials and any of the colloid photographic gelatin substitutes such as colloidal albumin, a cellulose derivative, or a synthetic resin for instance, a polyvinyl compound. Some colloids which may be used are polyvinyl alcohol or a hydrolyzed polyvinyl acetate as described in Lowe U.S. Patent 2,286,215, issued June 16, 1942; a far hydrolyzed cellulose ester such as cellulose acetate hydrolyzed to an acetyl content of 19–26% as described in U.S. Patent 2,327,808 of Lowe and Clark, issued August 24, 1943; a water-soluble ethanolamine cellulose acetate as described in Yutzy U.S. Patent 2,322,085, issued June 15, 1943; a polyacrylamide having a combined acrylamide content of 30–60% and a specific viscosity of 0.25–1.5 or an imidized polyacrylamide of like acrylamide content and viscosity as described in Lowe, Minsk and Kenyon U.S. Patent 2,541,474, issued February 13, 1951; zein as described in Lowe U.S. Patent 2,563,791, issued August 7, 1951; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in Unruh and Smith U.S. Patent 2,768,154, issued October 23, 1956; or containing cyano-acetyl groups such as the vinyl alcohol-vinyl cyanoacetate polymer as described in Unruh, Smith and Priest U.S. Patent 2,808,331, issued October 1, 1957; or a polymeric material which results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in U.S. Patent 2,852,382, of Illingsworth, Dann and Gates, issued September 16, 1958. If desired, compatible mixtures of two or more of these colloids may be employed.

The silver halide developing agent used can be any substituted cyclic nontanning developing agents used in photographic development processes. Silver halide developers that are used include 1-phenyl-3-pyrazolidone, any of the substituted 1-phenyl-3-pyrazolidones used as photographic developing agents, except those substituted with solubilizing groups, such as sulfonic acid groups, p-phenylenediamine, any of the substituted p-phenylenediamines used in photography, except those containing solubilizing groups, p-methylaminophenol sulfate and substituted p-methylaminophenol sulfates.

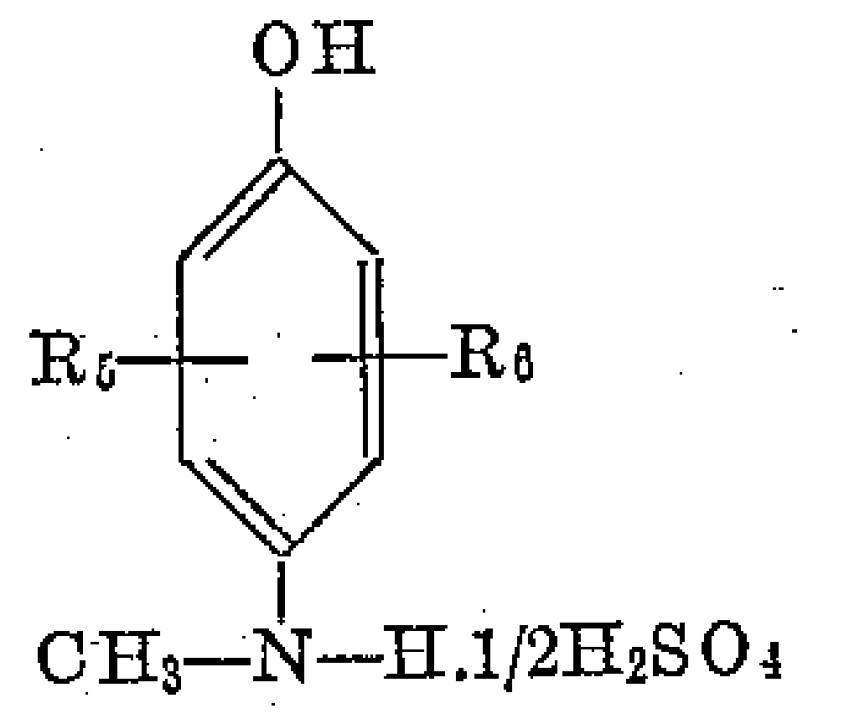
Among the preferred silver halide developing agents used in our photothermographic elements are (1) the 1-phenyl-3-pyrazolidones which may be represented by the formula:



wherein R_1, R_2, R_3 and R_4 may each represent a hydrogen atom, or an alkyl group having from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, butyl, secondary butyl, tertiary butyl, etc., so that not more than two of the R groups are alkyl groups; (2) the p-phenylenediamines which may be represented by the formula:



wherein R_5 and R_6 may each represent a hydrogen atom, or an alkyl group having from 1 to 16 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, amyl, tertiary amyl, hexyl, octyl, decyl, dodecyl, pentadecyl, hexadecyl, etc., and R_7 and R_8 each represent a hydrogen atom or an alkyl group containing from 1 to 16 carbon atoms as described for R_5 and R_6 or an alkylsulfonamidoalkyl group, for example, β-(methylsulfonamido)-ethyl, provided that not more than one group R_7 or R_8 represents an alkylsulfonamidoalkyl group; (3) the p-methylaminophenol sulfates which may be represented by the formula:



wherein R_5 and R_6 may each represent a hydrogen atom or an alkyl group having from 1 to 16 carbon atoms, such as methyl, ethyl, propyl, butyl, secondary butyl, tertiary butyl, tertiary amyl, hexyl, octyl, decyl, pentadecyl, hexadecyl, etc.; etc.

The 1-phenyl-3-pyrazolidone developing agents can be prepared by methods well known in the art, such as is described in Kendall U.S. 2,289,367, issued July 14, 1942. The p-phenylenediamines and p-methylaminophenol sulfates are all well known in the art.

Alkaline salts used in the silver halide developing layer are salts of strong bases and weak acids, for example, the alkali metal salts of weak acids preferably with water of crystalization such as sodium metaborate·$8H_2O$, potassium metaborate·$8H_2O$, etc., the salts of strong organic bases and weak acids, for example, the amine salts, such as isopropylamine acetate, isopropylamine oxalate, isopropylamine citrate, etc.

In addition to the developing agent, and alkali, the developer layer may contain various addends, such as saponin and other coating aids, sugar diacetyl, sodium sulfite, and other stabilizers, 1-phenyl-5-mercaptotetraazole, 5-methylbenzotriazole, and other antifoggants, etc., depending on the characteristics desired.

The light-sensitive silver halide emulsion may contain silver bromide, silver chloride, silver chlorobromide, silver iodide, silver bromoiodide, silver chloroiodide, etc.

The silver halide emulsion has a low sivler content which usually is about in the range of 4 mg. to 8 mg. of silver per square decimeter of the coated photothermographic element. The silver halide or mixed halide emulsion may be unsensitized, or it may be chemically sensitized, and/or optically sensitized with any of the sensitizers used in the art, such as those described in Dann et al., U.S. Serial No. 797,577, filed March 6, 1959, and now U.S. Patent 3,062,646.

The substantially water-insoluble alkali-permeable organic solvents used in the photothermographic element to dissolve the organic composition that changes color upon cross-oxidation, include any of the high boiling crystalloidal solvents, such as are listed in Mannes et al., U.S. Patents 2,304,939 and U.S. 2,304,940, both issued December 15, 1942, Jelley et al., U.S. 2,322,027, issued June 15, 1943, and others. Representative solvents include dibutyl phthalate, β-methoxyethyl phthalate, ethyl-N,N-di-n-butylcarbamate, tricresylphosphate, tri-p-tert. butylphenyl phosphate, triphenyl phosphate, ditetrahydrofurfuryl succinate, tetrahydrofurfuryl benzoate, N-n-amylphthalimide, N-n-amyl succinimide, ethylene glycol monobenzyl ether, glycol salicylate, etc. Among the organic solvents used in the elements according to our invention, are the liquid esters of higher monohydroxy alcohols and the waxy esters of alcohols which melt and become liquid in the temperature range used for the heat treatment and which solidify after this treatment.

The optimum ratio of solvent to binder used in making the element will depend upon the particular solvent used, the dye-formers and other factors. In general, this ratio must be sufficiently high to insure the transfer of adequate dye to produce a good image.

The substantially water-insoluble organic compositions which change color upon cross-oxidation with oxidized silver halide developing agents include:

I. The dye bases of the alkoxynaphthol series which are insoluble in water and which undergo the cross-oxidation reaction according to the invention, in particular methoxynaphthol, ethoxynaphthol, n-butoxynaphthol, sec. butoxynaphthol, tert. butoxynaphthol, etc.;

II. Any leuco dyes that are water-insoluble and undergo cross-oxidation reactions according to our invention, such as malachite green, crystal violet, auramine, p-rosaniline, indonaphthol blue and many others;

III. A mixture of

(*a*) A substantially water-insoluble substituted p-phenylenediamine having one primary amino group and having at least one higher alkyl substituent attached to the other amino group such as for example 2-amino-5-(N-ethyl-N-lauryl)aminotoluene, 2-amino-5-(N-ethyl-N-dodecyl)aminotoluene, 2-amino-5-(N-ethyl-N-pentadecyl)aminotoluene, etc., and

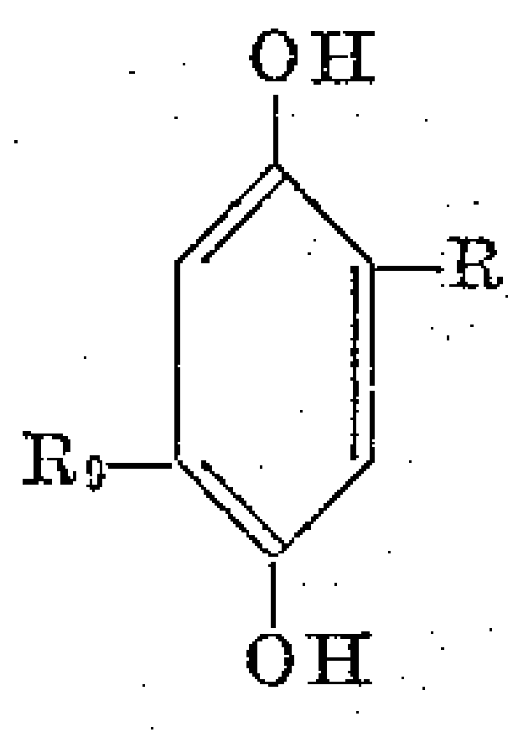
(*b*) A color forming coupler containing an active hydrogen such as

(1) Any cyan-dye-forming phenol or naphthol type couplers that have ballasting groups that make them water-insoluble; these include the following illustrative examples; the acylaminohydroxyphenol couplers of Porter et al., U.S. 2,346,080, issued April 4, 1944, such as 2-hydroxy-4′-[m-(p-tert. amylphenoxy)-benzamido]-diphenol, Salminen et al., U.S. 2,367,531, issued January 16, 1945, such as 2,6-di(4″-tert. amyl-3′-phenoxybenzoylamino)-1-phenol, 2-α(4′-tert. amylphenoxybutyryl)-amino)-5-chlorophenol, etc., the acylaminophenols of Salminen et al., U.S. 2,423,730, issued July 8, 1947, such as 2-(2′,4′-di-tert. amylphenoxyacetamido)-4,6-dichloro-5-methylphenol, 2-(4″-amylphenoxy-3-benzoylamido-3-chloro)phenol, etc., the 1-naphthol-2-carboxylic acid amide couplers of Weissberger et al., U.S. 2,474,293, such as 1-hydroxy-2[δ-(2′,4′-di-tert. amylphenoxy)-propyl] naphthamide, 1-hydroxy-2-{[β-(2′,4′-tert. diamyl phenoxy)acetamido]-ethyl}-naphthamide, etc.

(2) Any of the magenta-dye-forming 5-pyrazolone couplers having ballasting groups that render it water-insoluble, including the following illustrative examples; the 1-alkyl-3-acylamido-5-pyrazolones of Feniak et. al., U.S. 2,865,751, issued December 23, 1958, such as 1-dodecyl-3-[α-(2,4-di-n-amylphenoxy)acetamido]-5-pyrazolone, 1-dodecyl-3-{m-[α-(2,4-di-n-amylphenoxy)acetamido]-benzamido}-5-pyrazolone, etc., the 5-pyrazolone couplers of Feniak et al., U.S. 2,933,391, issued April 19, 1960, such as 1-(2,4,6-trichlorophenyl)-3-heptadecyl-5-pyrazolone, 1-(2,6-dichlorophenyl)-3-heptadecyl-5-pyrazolone, etc.

(3) Any of the yellow-dye-forming acylacetyl or acylacetanilide type couplers that are sufficiently ballasted to make them water-insoluble, including the following illustrative examples; the acylacetyl sulfonamide couplers of Weissberger, U.S. 2,350,138, issued May 30, 1944, such as p-benzoylacetamino-N-(p-toluenesulfonyl)-N-methylaniline, N-(p-benzoylacetaminobenzenesulfonyl)-N-benzyl-m-toluidine, etc., the benzoyl acetanilide couplers of McCrossen et al., U.S. 2,728,658, issued December 27, 1955, such as 4-(α-2′-methoxybenzoyl-α-chloroacetamido)-3″-(4‴-tert. amylphenoxy) benzanilide, etc., the couplers of McCrossen et al., U.S. 2,875,057, issued February 24, 1959, such as α-{4-[α-(2,4-di-tert. amylphenoxy) acetamido]benzoyl}-2-methoxyacetanilide, etc., etc.

IV. A substantially water-insoluble 2-alkyl-5-alkyl substituted hydroquinone having the formula:



wherein R_9 and R_{10} each represents an alkyl group having from 1 to 16 carbon atoms, such as methyl, ethyl, isopropyl, butyl, amyl, tertiary amyl, hexyl, octyl, decyl, dodecyl, pentadecyl, hexadecyl, etc. These compounds can be prepared as described in Crevling et al., U.S. Patent 2,899,334, issued August 11, 1959, and/or a corresponding substituted quinone (when both are used they are dispersed from separate solutions in organic solvent).

It has been found that the amount of the substituted hydroquinone present in the emulsion layer is a factor having an important effect on the formation of the quinhydrone. Too large an excess of the substituted hydroquinone reduces the rate at which the quinhydrone dye is formed, reduces the maximum density of the dye and may be detrimental to the stability of the dye image. It is, therefore, important to carefully adjust the amount of the substitued hydroquinone used in this dispersion. Although a somewhat wider range of proportions can be used, we have found it most advantageous to use the substituted hydroquinone in the range from 1.5 to 3 times the weight of silver in the silver halide emulsion.

The receiving paper should be both porous in order to carry along the maximum quantity of the water-insoluble alkali-permeable organic solvent at the time of transfer and sufficiently sized so that the dye does not continue to wander in the paper after transfer which would considerably lower definition. The choice of receiving paper depends on the organic solvent/gelatin ratio in the photothermographic element, on the temperature at which the transfer is made, the viscosity of the organic solvent containing the dye, etc. Baryta paper, for example, is the best receiver for transferring some di-n-butyl phthalate solutions of some dyes while the paper used for spirit duplicating purposes gives very acceptable copies.

The following representative examples will still further illustrate our photothermographic element and its use.

Example 1

On a 250 g. calendered baryta paper was coated a developer of the following composition.

Constituent:		Amount
Inert 20% gelatin solution	g.	100
Sugar solution, 80 g./l. water	g.	125
Saponine solution, 151 g./l. water	ml.	10
Diacetyl solution, 1.65 g./100 ml. water	ml.	10
Sodium metaborate, 8 moles water at 180 g./l.	ml.	100
Distilled water	ml.	100
5-methyl-1-phenyl-3-pyrazolidone	g.	2
Sodium sulfite, dry	g.	2
1-phenyl-5-mercaptotetrazole at 6.65 g./l. methanol	ml.	15

The pH of this composition was 9.70. It was coated at the rate of 60 mg. of dry material per square decimeter. The developer layer was dried, then the following emulsion was coated over it at 8 mg. of silver per square decimeter.

Constituent:		Amount
Silver chloride emulsion	g.	112.5
2-hexadecyl-5-methyl hydroquinone dispersion	g.	150
Distilled water	ml.	150
Saponine solution, 151 g./l.	ml.	7.5
Diacetyl solution, 1.65 g./100 ml.	ml.	7.5
Triethylene glycol	ml.	30

The dispersion of 2-hexadecyl-5-methyl hydroquinone had a composition of:

Constituent—		Amount
Gelatin in 8% solution	g.	375
Propylated naphthylene sulfonate (Alkanol B, manufactured by Du Pont)	g.	1.5
Dibutylphthalate	ml.	50
2-hexadecyl-5-methyl hydroquinone	g.	20

This coating was then dried.

Example 2

A photothermographic element was made as in Example 1 but replacing (1) the 5-methyl-1-phenyl-3-pyrazolidone and (2) the 1-phenyl-5-mercapto-tetrazole in the developer composition with (1) 2 g. of p-methylaminophenol sulfate and (2) 5 ml. of a solution of 39 g. of 5-methyl-benzotriazole in 100 ml. of methanol, respectively.

The photothermographic elements of Examples 1 and 2 were designed for exposure by contact printing, while the following example will illustrate an element designed for making enlargements of an original by projection exposure.

Example 3

On a 250 g. calendered baryta paper was coated a developer of the following composition.

Constituent:		Amount
Inert 20% gelatin solution	g.	100
Saponin solution, 151 g./l. water	ml.	10
Diacetyl solution, 1.65 g./100 ml. water	ml.	10
Distilled water	ml.	300
Isopropylamine acetate	g.	10
1-phenyl-3-pyrazolidone	g.	1
Sodium sulfite, dry	g.	1

The pH of this material was adjusted to 6.5 with acetic acid before coating. It was coated at the rate of 60 mg. of dry material per square decimeter. The developer layer was dried, then the following emulsion was coated over it at 4 mg. of silver per square decimeter.

Constituent:		Amount
Silver chlorobromide emulsion	g.	45
2-hexadecyl-5-methylhydroquinone dispersion	g.	35
Distilled water	g.	250
Saponin solution, 151 g./l. water	ml.	5
Diacetyl solution, 1.65 g./100 ml. water	ml.	5
Triethylene glycol	ml.	5
3-ethyl-5(3-methyl-2-thiazolinylidene ethylidene)-2-thio-2,4(3,5)-oxazole-dione (TTOD dye), 0.5 g./l. methanol	ml.	2

The dispersion of 2-hexadecyl-5-methylhydroquinone used in this emulsion had the composition below.

Constituent:		Amount
Gelatin in 8% solution	g.	200
Propylated naphthylene sulfonate (Alkanol B, manufactured by Du Pont)	g.	1
Dibutylphthalate	ml.	50
2-hexadecyl-5-methylhydroquinone	g.	20

This emulsion coating was then dried.

The preparation of dye negative images in a receiving sheet with our photothermographic elements is illustrated by the following example.

Example 4

A sample of the photothermographic elements of Example 1 was exposed by contact through a negative original in an office type copier, such as a Verifax Bantam Copier. The exposed sample was heat developed by passing it for about 15 seconds adjacent to a steam laundry iron and immediately applying a sheet of plain paper, such as is used in a spirit copying machine. After separating the receiving sheet from the developed element, the blue colored quinhydrone dye image became visible in about 30 seconds. This image was a negative of the original used to expose it. The hot developed element was contacted with another receiving sheet and a second copy of good quality was obtained after separating the paper as before.

Similarly a sample of the element made in Example 2 was exposed, developed and transferred to paper receiving sheets to make two copies of good quality.

A sample of the element from Example 3 was exposed with an enlarger by projecting an image on microfilm in reverse position to yield a print with a right reading image. The exposed element was heat developed and transferred as described above to produce good quality dye negative enlargements of the microfilm original.

Samples of the dye image copies upon prolonged exposure to ultraviolet light (125 w. lamp at 40 cm.) faded slowly with time. The whites of the copies remained unchanged. The keeping characteristics of the images were at least as good as the best prior art thermographic copies.

Direct positive copies can be prepared from an element of Example 3 by exposing and heat developing it as in Example 4 but substituting for the plain paper receiving sheet, a paper sheet containing the quinone of 2-hexadecyl-5-methyl-hydroquinone. However, to obtain good results, it is preferable to reduce the proportion of 2-hexadecyl-5-methylhydroquinone in the photothermographic element as is illustrated in the following representative example.

Example 5

A photothermographic element was made as in Example 3 but in which the emulsion composition was substituted by the following composition coated at 4 mg. of silver per square decimeter.

Constituent:		Amount
Silver chlorobromide emulsion	g.	45
2-hexadecyl-5-methylhydroquinone dispersion	g.	10
Distilled water	ml.	250
Saponin solution, 151 g./l. water	ml.	5
Diacetyl solution, 1.65 g./100 ml. water	ml.	5
Triethylene glycol	ml.	5

The dispersion of 2-hexadecyl-5-methylhydroquinone used in this composition was the same as used in Example 3.

The dried element was exposed by projection enlargement of a microfilm original, and heat developed as described in Example 4, then transferred to a previously heated receiving sheet (for use with a spirit duplicating machine) that was coated with 64 g. per square meter of the following composition:

2-hexadecyl-5-methylquinone	g.	2
Trichloroethylene	ml.	200

A good enlarged quinhydrone direct positive copy of the microfilm original was visible in the receiving sheet after it was separated from the photothermographic element and cooled. This copy showed the same desirable characteristics as the negative copy.

Example 6

On a 190 g. calendered baryta paper was coated a developer of the following composition.

Constituent:		Amount
Inert gelatin	g.	453
Water	ml.	3,812
Boric acid	g.	300
1-phenyl-3-pyrazolidone	g.	44.8
Sodium sulfite heptahydrate	g.	89.6
Saponin solution, 151 g./l.	ml.	300
Mucochloric solution, 26.6 g./l.	ml.	200
Isopropylamine (to adjust pH to 8.5)	ml.	170
Water, to make	g.	7,000

This solution was coated at the rate of 60 mg. of gelatin per square decimeter.

The developer layer was dried, then an emulsion of the following composition was coated over it at the rate of 5 mg. of silver per square decimeter.

Constituent:		Amount
Silver chlorobromide emulsion containing 1.5 atom-grams of silver and 200 g. of gelatin	g.	3,500
Dispersion C	g.	2,400
Saponin solution at 150 g./l.	ml.	400
Mucochloric acid solution at 26.6 g./l.	ml.	40
Triethyleneglycol	ml.	400
Methanol solution of TTOD dye at 0.5 g./l.	ml.	160
5-methylbenzotriazole sodium salt solution at 39 g./l.	ml.	200
Water, to make	g.	12,000

Dispersion C had the following composition.

Constituent:		Amount
Inert gelatin, 10% solution	g.	1,000
Alkanol B	g.	5.6
Water	ml.	160
Thymol aqueous alcoholic solution (50:50) at 21.5 g./l.	ml.	15
Water	ml.	100
2-hexadecyl-5-methylhydroquinone	g.	120
Dibutyl phthalate	ml.	300

To prepare Dispersion C, the gelatin solution, Alkanol B in aqueous solution, thymol in an aqueous alcoholic solution diluted with 100 ml. of water and substituted hydroquinone in solution in dibutyl phthalate were mixed in a high speed mixer for 1 minute.

The emulsion coating was rapidly dried and then conditioned under low relative humidity (30% to 40% R.H.).

A negative was copied on this element by projection exposure and then pressure applied on Verifax Copying Paper or on baryta paper to produce a positive copy (negative with respect to the original).

Example 7

This example relates to the production of a matrix sheet for obtaining a direct positive copy with an element containing a substituted quinone in the emulsion layer and 1-phenyl-3-pyrazolidone in the developer sublayer. In this case, the quinone was reduced by the nonoxidized developer in the undeveloped areas and, during transfer, such hydroquinone was transferred to such areas with an excess of quinone so as to give quinhydrone on the receiving sheet; while, in the exposed areas, only quinone was transferred to the receiving sheet, so that a direct positive copy was finally obtained.

On a 190 g. calendered baryta support was coated a developer having the following composition.

Constituent:	Amount
Inert gelatin	453 g.
Water	3,812 ml.
Boric acid	410 g.
Sodium acetate	110 g.
1-phenyl-3-pyrazolidone	45 g.
Sodium sulfite heptahydrate	22.5 g.
Sodium hydroxide solution at 100 g./l. (to adjust pH to 8.5)	About 1,100 ml.
Saponin solution at 150 g./l.	300 ml.
Mucochloric acid solution at 26.6 g./l.	200 ml.
Water, to make	7,000 g.

The constituents were added with stirring in the above order, to the aqueous solution of gelatin (453 g. of gelatin in 3,812 ml. of water) at 40° C. This composition was coated at a rate of 80 mg. of gelatin per square decimeter.

An emulsion coating of the following composition was then added.

Constituent:		Amount
Chloroiodide emulsion containing 1.15 atom-grams of silver	g.	4,200
Dispersion D	g.	3,200
Saponin solution at 150 g./l.	ml.	400
Mucochloric acid solution at 26.6 g./l.	ml.	200
Methanol solution at 0.5 g./l. of TTOD dye	ml.	160
Triethyleneglycol	ml.	400
Water, to make	g.	12,000

This composition was prepared by adding the constituents in the above order, with stirring, to the emulsion heated at 40° C.

Dispersion D had the following composition.

Constituent:		Amount
Solution at 10% of inert gelatin	g.	1,000
Alkanol B	g.	5.6
Water	ml.	160
Aqueous alcoholic solution (50:50) of thymol at 21.5 g./l.	ml.	15
Water	ml.	100
Dibutyl phthalate	ml.	300
2-Hexadecyl-5-methylquinone	g.	120

Dispersion D was prepared by stirring the constituents for 1 minute in a high speed mixer.

The emulsion coating was rapidly dried and then conditioned under low relative humidity (30% to 40% R.H.). This element was particularly designed for projection copying. Transfer was made onto a Verifax Copying Paper to obtain a direct positive copy.

Example 8

On a 190 g. calendered baryta paper was first coated a developer having the following composition.

Constituent:		Amount
Inert gelatin	g.	453
Water	ml.	3,812
Isopropylamine acetate	g.	453
N-methyl-para-aminophenol sulfate	g.	113
Sodium sulfite hepathydrate	g.	22.5
Hydroquinone	g.	67.5
Saponin solution at 150 g./l.	ml.	300
Mucochloric acid solution at 26.6 g./l.	ml.	200
Water, to make	g.	7,000

Before adding the water to make 7,000 g., the pH was adjusted to 7.

This material was coated at a rate of 80 mg. of gelatin per square decimeter and the coating was dried.

The following composition was then prepared by adding the various constituents in the above indicated order, with stirring, to the emulsion heated at 40° C.

Constituent:		Amount
Silver chloride emulsion containing 1.15 atom-grams of silver and 150 g. of gelatin	g.	2,000
Dispersion E	g.	1,600
Dispersion Q	g.	1,600
Saponin solution at 150 g./l.	ml.	400
Mucochloric acid solution at 26.6 g./l.	ml.	200
0.5% methanol solution of TTOD dye	ml.	160
Triethyleneglycol	ml.	200

This material was coated at a rate of 6 mg. per square decimeter.

Dispersions E and Q had the following compositions:

Constituent		Dispersion E	Dispersion Q
10% Solution of inert gelatin	g.	1,000	1,000
Alkanol B	g.	5.6	5.6
Water	ml.	100	100
50:50 Aqueous alcoholic solution of thymol at 21.5 g/l	ml.	15	15
Water	ml.	1,000	1,000
2-Hexadecyl-5-methylhydroquinone	g.	120	----------
2-Hexadecyl-5-methylquinone	g.	----------	60
Dibutyl phthalate	ml.	300	300

These dispersions were prepared by stirring their constituents for 1 minute in a high speed mixer.

The emulsion coating containing Dispersions E and Q was rapidly dried and then conditioned under low relative humidity (30% to 40% R.H.). By repeating the procedure of Example 4, except that a positive was copied instead of a negative, a quinhydrone direct positive image could be transferred onto Verifax Copying Paper.

Example 9

This example relates to the preparation of an image which is negative with respect to the original, by cross-oxidation between a leuco dye and the oxidation product of the developer.

On a 190 g. baryta paper was first coated a developer of the following composition.

Constituent:	Amount
Gelatin	453 g.
Water	3,812 ml.
Boric acid	410 g.
1-phenyl-3-pyrazolidone	22.4 g.
Sodium sulfite heptahydrate	22.4 g.
Spaonin solution at 150 g./l.	300 ml.
Mucochloric acid solution at 26.6 g./l.	300 ml.
Triethylene glycol	300 ml.
Sodium hydroxide solution at 100 g./l. (to adjust pH to 8.5)	About 1,100 ml.
Water, to make	7,000 g.

This solution was coated at a rate of 80 mg. of gelatin per square decimeter.

An emulsion of the following composition was then coated.

Constituent:		Amount
Silver chlorobromide emulsion containing 200 g. of gelatin and 1.15 atom-grams of silver	g.	3,500
Dispersion F	g.	6,000
Saponin solution at 150 g./l.	ml.	400
Muchochloric acid solution at 26.6 g./l.	ml.	100
Triethyleneglycol	ml.	400
5-methylbenzotriazole sodium salt solution at 39 g./l.	ml.	160
Methanol solution at 0.5 g./l. of TTOD dye	ml.	160

To prepare this composition, the constituents were added with stirring in the above order to the silver chlorobromide emulsion heated at 40° C.

Dispersion F had the following composition.

Constituent:		Amount
Inert gelatin, 10% solution	g.	1,000
Alkanol B	g.	5.6
Water	ml.	160
50:50 aqueous alcoholic solution of thymol at 21.5 g./l.	ml.	15
Water	ml.	100
Glycol salicylate	ml.	450
Leuco Indonaphthol Blue	g.	60

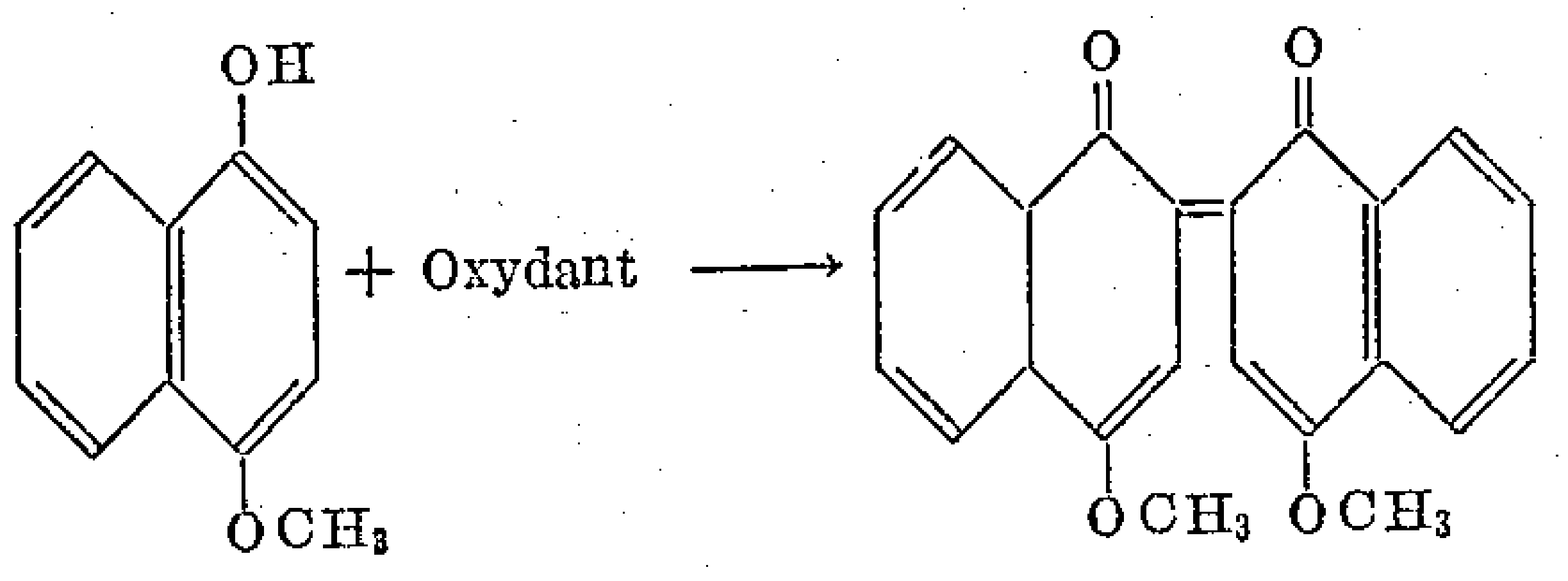
This dispersion was prepared by stirring its constituents in a high speed mixer for 1 minute.

The composition was coated, the resulting coating was rapidly dried and then conditioned under low relative humidity (30% to 40%).

A negative was copied by projection exposure on the resulting element; and, after heat development as previously indicated, it was pressure applied on Verifax Copying Paper to yield a positive copy (negative with respect to the original).

Example 10

This example relates to an embodiment of the invention utilizing the formation of Russig Blue from methoxynaphthol according to the reaction.



On a 190 g. calendered baryta paper was coated a material of the following composition.

Constituent:		Amount
Inert gelatin	g.	453
Water	ml.	3,812
Isopropylamine acetate	g.	453
1-phenyl-3-pyrazolidone	g.	45
Sodium sulfite heptahydrate	g.	22.5
Mucochloric acid solution at 26.6 g./l.	ml.	200
Saponin solution at 150 g./l.	ml.	300
Water, to make	g.	7,000

The constituents were added with stirring in the above order to the gelatin solution heated at 40° C.

This composition was coated at a rate of 80 mg. of gelatin per square decimeter.

On this layer was then coated an emulsion of the following composition.

Constituent:		Amount
Silver chlorobromide emulsion containing 200 g. of gelatin and 1.15 atom-grams of silver	g.	3,500
Dispersion G	g.	4,000
Saponin solution at 150 g./l.	ml.	400
Mucochloric solution at 26.6 g./l.	ml.	800
Methanol solution at 0.5 g./l. of TTOD sensitizing dye	ml.	160
Triethyleneglycol	ml.	400
Water, to make	g.	12,000

Dispersion G was prepared by stirring the following constituents for 1 minute in a high speed mixer.

Constituent:		Amount
Inert gelatin, 10% solution	g.	1,000
Alkanol B	g.	5.6
Water	ml.	160
Aqueous alcoholic solution (50:50) of thymol at 21.5 g./l.	ml.	15
Water	ml.	100
Methoxynaphthol	g.	60
Dibutyl phthalate	ml.	300

The emulsion was prepared by mixing its constituents with stirring, the silver chlorobromide emulsion being initially at 40° C.

The coatings were rapidly dried and then conditioned under relative humidity (30% to 40%).

A negative was copied on the resulting element; and, after heat development in the presence of moisture, it was pressure applied on Verifax Copying Paper to obtain a positive copy (negative with respect to the original).

Example 11

This example relates to an embodiment of the invention which utilizes, for forming the dye, a reaction between the oxidation product of a developer of the para-phenylenediamine type and a color-forming coupler.

On a 190 g. calendered baryta paper was first coated a material of the following composition.

Constituent:	Amount
Inert gelatin	453 g.
Water	3,812 ml.
Boric acid	410 g.
1-phenyl-3-pyrazolidone	22.4 g.
Sodium sulfite heptahydrate	44.8 g.
Saponin solution at 150 g./l.	300 ml.
Mucochloric acid solution at 26.6 g./l.	200 ml.
Triethyleneglycol	300 ml.
Sodium hydroxide solution at 100 g./l. (to adjust pH to 8.5)	About 1,100 ml.
Water, to make	7,000 g.

To the gelatin solution at a temperature of 40° C., the other constituents were successively added in the above order, with constant stirring. This material was coated at a rate of 60 mg. of gelatin per square decimeter and then dried.

A material of the following composition was then coated.

Constituent:		Amount
Silver chlorobromide emulsion containing 200 g. of gelatin and 1.15 atom-grams of silver	g.	3,500
Dispersion H	g.	4,000
Saponin solution at 150 g./l.	ml.	400
Mucochloric solution at 26.6 g./l.	ml.	100
Triethyleneglycol	ml.	400
Methanol solution of TTOD dye at 0.5 g./l.	ml.	160
5-methyl-benzotriazole sodium salt solution at 39 g./l.	ml.	160
Water, to make	g.	12,000

The silver chlorobromide emulsion being at 40° C., the other constituents were successively added in the above order with constant stirring.

Dispersion H was prepared by placing the following constituents in a high speed mixer and by stirring for 1 minute.

Constituent:		Amount
Inert gelatin, 10% solution	g	1,000
Alkanol B	g	5.6
Water	ml	160
Aqueous alcoholic solution (50:50) of thymol at 21.5 g./l.	ml	15
Water	ml	100
2 - (2',4' - diamylphenoxyacetamino) - 4,6 - dichloro-5-methylphenol	g	150
Dibutyl phthalate	ml	240
2 - methyl - 5 - (N - ethyl - N-lauryl)-aminotoluene	g	30
Dibutyl phthalate	ml	30

The emulsion was coated at a rate of 6 mg. of silver per square decimeter. It was then rapidly dried and conditioned under low relative humidity (30% to 40%).

A negative was copied by projection on this element; and, after heat development in the presence of moisture, it was pressure applied on spirit duplicating paper, and a positive copy was finally obtained (negative with respect to the original).

Our invention is still further illustrated by reference to the accompanying drawing that contains FIGS. 1, 2 and 3 which show greatly enlarged across sections of our photothermographic element with the original image or with a receiving sheet.

FIG. 1 shows light source 10 printing through the original image 11 onto the photothermographic element comprising light-sensitive silver halide emulsion layer 12 containing 2-hexadecycl-5-methylhydroquinone that is coated over layer 13 which contains 1-phenyl-3-pyrazolidone and isopropylamine acetate which, in turn, is coated on support 14.

FIG. 2 shows the plain paper receiving sheet 15 which has been contacted with layer 18 of the hot developed photothermographic element, said layer containing the 2-hexadecycl-5-methylquinone, 2 - hexadecyl - 5-methylhydroquinone and silver negative image 17, then separated from the layer, allowed to cool to obtain the quinhydrone dye negative image 16 in receiving sheet 15 formed from the 2-hexadecycl-5-methylhydroquinone and 2-hexadecyl-5-methylquinone transferred from layer 18.

FIG. 3 shows the 2-hexadecyl-5-methylquinone coated paper receiving sheet 19 which has been contacted with layer 18 of the hot developed photothermographic element, then separated from the element and allowed to cool to obtain the 2-hexadecyl-5-methylquinhydrone dye positive image 20 formed by the transfer of unused 2-hexadecyl-5-methylhydroquinone to receiving sheet 19 where it reacted with the 2-hexadecyl-5-methylquinone of sheet 19.

The novel photothermographic elements of our invention are valuable for making stable dye image copies of an original image by contact or projection printing, or by exposure in a camera of the Photostat copier type, followed by a rapid, and simple heat process with a subsequent transfer step. The transferred dye images on the copies are substantially free of processing chemicals and unused silver halide, and therefore have optimum stability. Cross-oxidation reactions are utilized which take place only under the conditions of heat processing. Since these reactions take place at much lower pH levels than would be required in conventional color-forming reactions, the pH of the developing layer of the element is relatively low and results in elements having better stability than would otherwise be possible. Some of the elements processed according to our invention produce negative dye images and the others produce positive dye images of the original.

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 as described hereinabove and as defined in the appended claims.

We claim:

1. A light-sensitive photothermographic element comprising:
   - (*a*) a support, coated with
   - (*b*) a first layer comprising a hydrophilic colloid binder; an alkaline salt selected from the class consisting of an alkali metal salt of a weak acid and an amine salt of a weak acid; and a nontanning silver halide developing agent selected from the class consisting of a 1-phenyl-3-pyrazolidone, a p-phenylenediamine, and a p-methylaminophenol; and coated over said layer,
   - (*c*) a second layer comprising a hydrophilic colloid; a dispersion of light-sensitive silver halide; and a solution of a substantially water-insoluble compound selected from the class consisting of a 2-alkyl-5-alkylhydroquinone and a 2-alkyl-5-alkylquinone, dissolved in a substantially water-insoluble alkali-permeable solvent selected from the class consisting of liquid esters of higher monohydroxy alcohols and the waxy esters of alcohols which melt and become liquid in the temperature range of from about 70° C. to about 100° C.

2. A light-sensitive photothermographic element of claim 1 in which the second layer includes a solution of a 2-alkyl-5-alkylquinone dissolved in a substantially water-insoluble, alkali-permeable solvent selected from the class consisting of liquid esters of higher monohydroxy alcohols and the waxy esters of alcohols which melt and become liquid in the temperature range of from about 70° C. to about 100° C., when the solution in the second layer of said element contains a 2-alkyl-5-alkylhydroquinone.

3. A light-sensitive photothermographic element comprising:
   - (*a*) a paper support, coated with
   - (*b*) a first hydrophilic colloid layer comprising a binder, sodium metaborate$\cdot 8H_2O$ and 5-methyl-1-phenyl-3-pyrazolidone and coated over said layer,
   - (*c*) a second hydrophilic colloid layer comprising a binder having dispersed therein light-sensitive silver halide and 2-hexadecyl-5-methyl hydroquinone dissolved in dibutylphthalate.

4. A light-sensitive photothermographic element comprising:
   - (*a*) a paper support, coated with
   - (*b*) a first hydrophilic colloid layer comprising a binder, sodium metaborate$\cdot 8H_2O$ and 1-phenyl-3-pyrazolidone and coated over said layer,
   - (*c*) a second hydrophilic colloid layer comprising a binder having dispersed therein light-sensitive silver halide and 2-hexadecyl-5-methylquinone dissolved in dibutylphthalate.

5. A light-sensitive photothermographic element comprising:
   - (*a*) a paper support, coated with
   - (*b*) a first hydrophilic colloid layer comprising a binder, isopropylamine acetate and p-methylaminophenol sulfate and coated over said layer,
   - (*c*) a second hydrophilic colloid layer comprising a binder having dispersed therein light-sensitive silver halide, 2-hexadecyl-5-methylhydroquinone dissolved in dibutylphthalate and 2-hexadecyl-5-methylquinone dissolved in dibutylphthalate.

6. A process for producing a copy containing a colored image of an original image with a light-sensitive photo-

thermographic element that contains a latent image of said original image, said element comprising:

(*a*) a support, coated with

(*b*) a first layer comprising a hydrophilic colloid binder; an alkaline salt selected from the class consisting of an alkali metal salt of a weak acid and an amine salt of a weak acid; and a nontanning silver halide developing agent selected from the class consisting of a 1-phenyl-3-pyrazolidone, a p-phenylenediamine, and a p-methylaminophenol; and coated over said layer,

(*c*) a second layer comprising a hydrophilic colloid; a dispersion of light-sensitive silver halide; and a solution of a substantially water-insoluble compound selected from the class consisting of a 2-alkyl-5-alkylhydroquinone and a 2-alkyl-5-alkylquinone, dissolved in a substantially water-insoluble alkali-permeable solvent selected from the class consisting of liquid esters of higher monohydroxy alcohols and the waxy esters of alcohols which melt and become liquid in the temperature range of from about 70° C. to about 100° C.;

said process comprising the steps:

(1) treating said photothermographic element containing the latent image with steam to raise its temperature to the range of from about 70 to about 100° C. so that the nontanning developing agent develops the light exposed areas of said latent image to a silver image and forms corresponding areas of oxidized nontanning silver halide developer against a background of unoxidized nontanning developer which cross-oxidizes the said water-insoluble compound selected from the class consisting of a 2-alkyl-5-alkylhydroquinone and a 2-alkyl-5-alkylquinone to produce the corresponding 2-alkyl-5-alkylquinhydrone dye image;

(2) transferring the said 2-alkyl-5-alkylquinhydrone dye image to a paper receiving sheet by contacting said second layer of said hot element with said paper receiving sheet; and

(3) separating said receiving sheet from said hot element leaving said 2-alkyl-5-alkylquinhydrone dye image reproduction of said original on said receiving sheet.

7. A process for producing a copy containing a quinhydrone negative image of an original with a light-sensitive photothermographic element comprising:

(*a*) a paper support, coated with

(*b*) a first hydrophilic colloid layer comprising a binder, sodium metaborate$\cdot 8H_2O$ and 5-methyl-1-phenyl-3-pyrazolidone and coated over said layer,

(*c*) a second hydrophilic colloid layer comprising a binder having dispersed therein light-sensitive silver halide and 2-hexadecyl-5-methylhydroquinone dissolved in dibutylphthalate,

said process comprising the steps:

(1) exposing the said element to light through an original image,

(2) treating said exposed element to steam to raise its temperature to the range of from 70 to 100° C.,

(3) contacting the second colloid layer of the said hot element with a plain paper receiving sheet, and

(4) separating said receiving sheet from said hot element leaving a quinhydrone negative image of the said original on the cooled receiving sheet.

8. A process for producing a copy containing a quinhydrone positive image of an original with a light-sensitive photothermographic element comprising:

(*a*) a paper support, coated with

(*b*) a first hydrophilic colloid layer comprising a binder, sodium metaborate$\cdot 8H_2O$ and 5-methyl-1-phenyl-3-pyrazolidone and coated over said layer,

(*c*) a second hydrophilic colloid layer comprising a binder having dispersed therein light-sensitive silver halide and 2-hexadecyl-5-methylhydroquinone dissolved in dibutylphthalate,

said process comprising the steps:

(1) exposing the said element to light through an original image,

(2) treating said exposed element to steam to raise its temperature to the range of from 70 to 100° C.,

(3) contacting the colloid layer of the said hot element with a paper receiving sheet that contains 2-hexadecyl-5-methylquinone, and

(4) separating said receiving sheet from said hot element leaving a quinhydrone positive image of said original on the cooled receiving sheet.

9. A process for producing a copy containing a quinhydrone positive image of an original with a light-sensitive photothermographic element comprising:

(*a*) a paper support, coated with

(*b*) a first hydrophilic colloid layer comprising a binder sodium metaborate$\cdot 8H_2O$ and 1-phenyl-3-pyrazolidone and coated over said layer,

(*c*) a second hydrophilic colloid layer comprising a binder having dispersed therein light-sensitive silver halide and 2-hexadecyl-5-methylquinone dissolved in dibutylphthalate,

said process comprising the steps:

(1) exposing the said element to light through an original image,

(2) treating said exposed element to steam to raise its temperature to the range of from 70 to 100° C.,

(3) contacting the colloid layer of the said hot element with a paper receiving sheet, and

(4) separating said receiving sheet from said hot element leaving a quinhydrone positive image of said original on the cooled receiving sheet.

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