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PRODUCTION OF DIRECT POSITIVE IMAGES AND LIGHT SENSITIVE ELEMENT THEREFOR

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This invention pertains to new photographic materials and to new processes for the direct formation of positive images and relief images. More particularly, it pertains (*a*) to photographic films, plates and papers bearing a novel photosensitive layer comprising a water-permeable colloid binder and a dispersed liquid mixture of a thiol and an ethylenically unsaturated compound and, if desired, an addition polymerization initiator activatable by actinic light, (*b*) to processes for the production of direct positive images therefrom, and (*c*) to processes for the production of printing plates.

A considerable amount of research and development work has been, and is being, done in an effort to provide economical photosensitive materials and simple processes for image reproduction including the direct formation of positive images. For example, the stencil and spirit duplication, offset duplication, and diazo processes have been known for years and have various disadvantages. For instance, offset duplication is complicated, requires skilled operators, and is economically useful only in the production of about 500 or more copies. The diazo process is practical only when a relatively small number of positives is required. The copies fade and the speed of reproduction is relatively slow. The gelatin process likewise is practical for the production of only a small number of copies and, furthermore, the original master is useful only for a short time after formation.

A process based on a sensitized paper which is selectively acted upon by light passed through the back thereof and reflected from the light and dark areas of the original is used commercially. However, duplication from the master, or matrix, depends on transfer of dye by pressure after the exposed matrix has been activated in a suitable solution. Only a few copies can be made from the matrix, and critical operator judgment is required to determine proper exposure, development, and roller pressure.

Another commercial process utilizes a positively electrically charged, selenium-coated plate in a camera. Copying from the exposed plate, which in the exposed areas no longer contains charged selenium particles, is accomplished by the use of a negatively charged, black, resinous powder and a positively charged sheet of paper for the final print which is fixed or fused by heat. Certain disadvantages include the tendency of particles to adhere to the blank areas of the copy paper, resulting in dirty background and non-uniform areas, especially large, solid colored areas. Furthermore, since the process is electrostatic in nature, changes in humidity cause electrical leakage and loss of static charge on the plate or copy.

Another process is known in which material to be duplicated is placed beneath a paper which is sensitive to heat. The combination is subjected to infrared light. The printed, or written, material being dark absorbs the light and converts the light rays to heat. The special paper is darkened where it is exposed to heat, and the original image is, in effect, burned into the copy paper.

Still other processes are based on photoelectric scanning and production of color by controlled activation with electric current of chemically treated paper; on the attraction of electrically charged, dry, smoke particles to a photoconductive plate on which the image is projected optically; or on ferromagnetic processes involving the formation of magnetic images on sheets of permanent magnetic material by a magnetic stylus, driven by a photoelectric system scanning the printed original.

As is apparent from the above discussion, widely varied systems of producing direct positives are known. However, no economical versatile process has as yet been provided. Furthermore, none of the known processes enable one to produce at the same time a direct positive and a positive duplicating matrix.

An object of this invention is to provide a new type of photographic material which is economical to make and use. Another object is to provide such material, e.g., films, plates and papers from which good positive images can be formed directly. Yet another object is to provide such material which can be used to reproduce images from various image-bearing materials including process negatives, continuous tone transparencies, semi-opaque copy materials including paper with drawings, type matter or typewritten matter thereon. A further object is to provide such material which utilizes commercially available and economical chemicals. A still further object is to provide such materials which can be used to produce either direct positive prints or positive duplicating matrices or other relief images. Still further objects will be apparent from the following description of the invention.

The above objects are attained in accordance with this invention which in one important aspect comprises a suitable support and a photosensitive layer comprising a water-sensitive, that is, water-soluble or water-permeable, organic colloid of high molecular weight possessing protective colloid properties having intimately dispersed therethrough a liquid mixture of a thiol and an ethylenically unsaturated compound reactive with said thiol upon irradiation with actinic light.

Although the wave length of the radiation used may be selcted so that the mercaptan/ethylenically unsaturated compound composition is activated per se, generally through the mercaptan component, it is usually desirable to use an added photosensitizer. The addition polymerization initiators activatable by actinic light comprise a useful class of such photosensitizers. These are used in amounts ranging from 0.01% to 10% by weight of the photosensitive layer. In general, the colloid is present in an amount from 35 to 85%, the thiol in 5 to 35% and the unsaturated compound from 5 to 35%, all by weight of the layer.

The novel processes of the invention in their broader aspects comprise (*a*) exposing to actinic light selected areas of the photosensitive layer described in the previous paragraph and (*b*) developing the exposed film, e.g., by treating it with an aqueous solution of a metal salt, the metal ion of which forms an insoluble product with said thiol, whereby a positive monocolor image is developed in said film. In those instances where the metal ion/thiol reaction product is a hardener for the binder, the exposed areas, i.e., the clear areas, of the color image can be removed if desired by treatment with a suitable solvent therefor in which the color image areas are insoluble, whereby a positive, colored, height relief suitable for master matrix use in duplication is obtained.

The water-permeable organic colloid binders useful in the layers include those which have protective colloid properties and which are freely permeable to water and aqueous solutions. Thus, they have molecular weights in excess of 5000, hydrophilic properties in the form of thin films, and form adherent solid films. The useful colloid binding agents include those useful as binding agents for silver halide grains in photographic emulsions and include both natural and synthetic organic colloids and mixtures of such colloids, e.g., gelatin, albumin, agar-agar, casein, alginic acid and the alginates; gums, such as gum tragacanth and gum arabic; polyvinyl alcohol and its carboxylic acid esters and acetals which con-

tain sufficient free hydroxyls to confer hydrophilic character, e.g., the acetals with formaldehyde, acetaldehyde, butyraldehyde, sodium o-sulfobenzaldehyde, and color-forming acetals; cellulose derivatives, including nitrocellulose and water-soluble or hydrophilic cellulose derivatives, for instance, cellulose glycollic acid, methyl and ethyl cellulose, water-soluble or hydrophilic polycarboxamides, and polyvinylpyrrolidones.

The photosensitive layer for the elements can be made in various manners by admixing the ingredients and a suitable solvent or solvents, and the resulting viscous solution or dispersion is then coated, cast or extruded onto the surface of a suitable support and dried. For example, the ethylenically unsaturated compound and the thiol can be dissolved in a small quantity of a water-miscible volatile organic solvent, e.g., acetone, and the solution dispersed by stirring it into an aqueous solution of the water-soluble or water-permeable protective colloid of high molecular weight. The intimate dispersion of the liquid mixture of a thiol and the ethylenically unsaturated compound (or mixtures thereof) complementarily reactive therewith on irradiation can be a true liquid/solid dispersion or it can be a complete molecular dispersion, i.e., a solution of the liquid mixture in the protective colloid.

Generally speaking, in the case of the commonly available natural protective colloids, such as gelatin, it will be preferred to have the liquid mercaptan/unsaturate mixture substantially uniformly particulately dispersed as a liquid mixture in the solid binder. The photographic speed of such particulate liquid/solid dispersions generally increases as the size of the liquid mixture particles decreases. In the case of the synthetic protective binder colloids, for instance, polyvinyl alcohol, the liquid mixture of the thiol and complementarily reactive unsaturate can be uniformly, molecularly dispersed in true solution form within the binder colloid.

Photosensitizing agents can also be present in the layer, and in some instances are quite beneficial. Desirably, the overall composition is rendered as free of oxygen as possible, although this is not necessary. The unsensitized compositions will generally show greatest response to actinic light of wave lengths less than 3000 A. By the addition of appropriate photosensitizers the composition can be modified to respond to radiation of the near ultraviolet, the visible spectrum, or even to X-rays. Suitable choice of the added photosensitizers will result in compositions which are activatable only by actinic light of selected wave lengths, for instance, those capable of activation only by X-rays which would therefore be handleable both as to preparation and development in daylight. A useful class of such photosensitizers are the addition polymerization initiators activatable by actinic light, which are well known as a class in the addition polymer art as compounds capable of the generation of radicals on irradiation with actinic light.

Suitable supports include paper of all the types used for making diazo papers and photographic silver halide coated papers, as well as metals, e.g., steel and aluminum plates, sheets and foils, and films or plates composed of various film-forming synthetic resins or high polymers, such as the addition polymers, including the vinylidene polymers, e.g., the vinyl chloride polymers, vinylidene chloride copolymers with vinyl chloride, vinyl acetate, styrene, isobutylene and acrylonitrile; and vinylchloride copolymers with the latter polymerizable monomers; the linear condensation polymers such as the polyesters, e.g., polyethylene terephthalate; the polyamides, e.g., polyhexamethylene sebacamide; polyester amides, e.g., polyhexamethylene-adipamide/adipate; etc. Fillers or reinforcing agents can be present in the synthetic resin or polymer bases such as the various fibers (synthetic, modified, or natural), e.g., cellulosic fibers, for instance, cotton, cellulose acetate, viscose rayon, paper; glass wool; nylon, and the like. These reinforced bases may be used in laminated form.

Light sources for the exposure may vary widely and include those used for making diazo prints. Suitable sources include tungsten filament lamps, carbon arcs, mercury vapor arcs, fluorescent lamps with special ultra violet light emitting phosphors, argon glow lamps and photoflood lamps. When photosensitizers sensitive to visible or near ultraviolet light, e.g., addition polymerization initiators, are present, mercury vapor lamps, particularly the sunlamp type and fluorescent sun lamps, are most suitable.

The following examples in which the parts given are by weight, unless otherwise specified, are submitted to illustrate further but not to limit this invention. The compositions are made and coated in the substantial absence of actinic radiations to prevent exposure prior to the intended photographic exposure during use. Normal room light is not actinic for many of these compositions varying with the photosensitizer, if any.

Example I

A solution of 4 parts of 1-decene, 1 part of n-dodecyl mercaptan, and 1 part of acetone was dispersed in a warm aqueous gelatin solution and the resultant dispersion cast on a glass plate and allowed to set. The resultant, solid gelatin film containing an intimate dispersion of the liquid decene/mercaptan/acetone composition was then partly masked and exposed to the light from a commercial, 1000-watt, high pressure, quartz-jacketed, water-cooled mercury arc for a period of 20 minutes. The mask was then removed and the exposed plate covered with a saturated aqueous solution of lead nitrate. The film in the exposed areas remained colorless; whereas, the film in the unexposed areas, i.e., those areas underneath the mask, became yellow.

An identical dispersion was prepared, omitting the 1-decene, and a film prepared therefrom was partly masked and exposed as above for 60 minutes. Development with lead nitrate solution as before revealed no contrast. Both exposed and unexposed areas of the film turned the same shade of yellow, thereby demonstrating the necessity of the olefin for image formation.

Another film was prepared from a further sample of the 1-decene/dodecyl mercaptan/acetone/gelatin dispersion and exposed in masked steps to the mercury arc for periods of 5, 15, 30, 60, 120, 240, 480, 960, and 1920 seconds. After the stepped exposure, the film was developed as before with lead nitrate solution. No yellow color was observed in areas of the film exposed for periods of 240 seconds or more. Exposed areas of the film could be differentiated from non-exposed areas after development with an exposure of 60 seconds or more. These results indicate adequate image formation with an exposure of 60 seconds or more and maximum contrast with an exposure of 240 seconds.

Example II

An emulsion of 2 parts of 1-decene, 1 part of n-dodecyl mercaptan, and a small amount of benzoin was prepared in warm aqueous gelatin and a film cast therefrom, all as in Example I. The resultant dried film was exposed in a series of masked steps to the same light source as in Example I. After development with aqueous lead nitrate solution, the masked step areas showed no yellow color appearing in areas of the film exposed for 120 seconds or more; exposed areas could be differentiated from unexposed areas with exposures of 30 seconds or more. These results indicate an increase in photographic speed with decreasing ratio of 1-decene to the dodecyl mercaptan and substitution of benzoin for acetone. Thus, adequate image formation can be obtained with exposures as short as 30 seconds, and maximum contrast is obtained with exposures of 120 seconds.

Another sample of the film was prepared and exposed

in increasing masked steps and developed with aqueous salt solutions containing Pb^{++}, Co^{++}, and Cu^{++} ions. The exposed areas developed with the Pb^{++} solution gave the best color images—a good contrast in yellow. The exposed areas developed with the Co^{++} solution gave a deep red image of satisfactory contrast. The exposed areas developed with the Cu^{++} solution gave a greenish yellow image of fairly low contrast.

Example III

Film strips were prepared as in Example I from warm aqueous gelatin, 1-decene, n-dodecyl mercaptan, and a dilute aqueous soap solution containing small quantities of acetone and benzoin in the following relative amounts:

	Dilute Aqueous Soap Solution Containing Small Quantities of Acetone and Benzoin, parts	n-Dodecyl Mercaptan, parts	1-Decene, parts
Strip 1	20	2	10
Strip 2	20	5	10
Strip 3	20	7	7
Strip 4	20	10	5

Each strip was successively masked and exposed in stepped wedges for periods of 5, 15, 30, 60, 120, 240, 480, 960 and 1920 seconds to the light from the mercury arc described in detail in Example I, filtered through a high silica filter which passed no radiation at wave lengths lower than 2100 A. The films were developed with aqueous lead nitrate solution. The speed of image formation was greatest in Strip 3 in which the mercaptan to olefin ratio was substantially 1:1.

Example IV

Another film was prepared as in Example III, using the proportions given for Strip 4. A portion of the film was exposed with suitable masking for intervals of 5, 10, 20, 40, 60, 120, 240, and 480 seconds, respectively, and the remainder of the film was exposed through an image-bearing transparency to the unfiltered light from the light source described in Example I. A portion of the film was developed with an aqueous Pb^{++} solution and the remainder with aqueous Co^{++} solution, divided such that the stepped wedges were developed with each solution. The exposed film could be distinguished from the unexposed film after exposures of 20 seconds or more with development by either the Pb^{++} or Co^{++} solution, i.e., a suitable color image was obtained with an exposure of twenty seconds. The area corresponding to the pattern of radiation for the fixe-minute exposure was developed with a Pb^{++} solution and a sharp image of the pattern was obtained.

Example V

A solution of 0.84 part of n-dodecyl mercaptan, 0.585 part (equimolar based on mercaptan) of 1-decene and 0.05 part of benzoin methyl ether was dispersed by means of a valve homogenizer in 70 parts of a warm 5% solution of gelatin in water. Portions of the warm dispersion were coated onto glass plates and onto paper. After gelling and drying, the photosensitive coatings on glass were translucent with a smooth matte surface and those on paper were smooth with a slight gloss. Coatings on both glass and paper were given stepped exposures ranging from 0.5 to 15 minutes under a line negative to the light from two 15-watt BL–360 fluorescent lamps at a distance of 3 inches from the plane of the negative. After exposure and development for 5 minutes in a 5% aqueous solution of lead acetate, sharp images were visible in all exposure steps of both the plate and the paper. The unexposed areas were bright yellow while the exposed areas were lighter yellow or colorless depending on the extent of exposure and on the coating weight. In general, the exposed areas were completely colorless at exposures of 5 minutes or longer.

One of the coatings on glass was given a stepped exposure of 5, 10, and 15 minutes and then developed in a 5% cobalt nitrate hexahydrate solution for 25 minutes. A sharp but very pale orange image was obtained initially. On standing overnight in air, the orange image darkened to a deep red color. The exposed areas were light pink to colorless depending on the extent of the exposure.

On treatment of such a developed plate with warm water, the gelatin in the exposed areas was washed away leaving a colored, height relief image corresponding to the letter text in the opaque areas of the original line negative. Similar treatment of an exposed plate which had been developed in lead acetate so as to give lead mercaptide in the unexposed areas dissolved completely in the warm water, indicating that the hardening observed above was due to the presence of the cobalt.

Other reactions which give colored products with mercaptans can also be used for the development step. For example, a coating prepared and exposed essentially as above was bathed in a 1% aqueous solution of sodium nitro-prusside for 1–2 minutes after which the bath was made alkaline by addition of a sodium hydroxide solution. A fugitive, reddish purple image of the text in the opaque areas of the negative was developed in the unexposed areas.

Example VI

To a solution of 5 parts of a hydrolyzed ethylene/vinyl acetate copolymer (about 5% ethylene) in 50 parts of water and eight parts of ethanol there was added a solution of 0.75 part of potassium carbonate and 1 part of 2-mercaptoacetic acid in 10 parts of water followed by a solution of 2.5 parts (substantially equimolar on acid) of potassium p-styrenesulfonate and 0.1 part of sodium 2-anthraquinonesulfonate in 10 parts of water. The solution was coated onto glass plates and allowed to dry. A hazy, white, photosensitive layer was obtained. Upon exposure for 20 minutes under a line negative to the light from three RS sunlamps at a distance of eight–nine inches and subsequent development in a 5% aqueous solution of cobalt nitrate hexahydrate, there was obtained a faint brown negative image of the text (i.e., brown in the unexposed areas corresponding to the opaque areas in the negative). The plate was then rinsed in water and dried. On standing overnight, the faint brown image deepened to a dark chocolate color. The exposed areas were not entirely colorless.

Example VII

A solution of 1.26 parts of n-dodecyl mercaptan 1.35 parts (about 2.0 molar on mercaptan) of styrene, and 0.1 part of benzoin methyl ether was dispersed by means of a valve homogenizer in 75 parts of a warm 10% gelatin solution. The dispersion was coated onto glass plates, allowed to gel, and dried. The dry photosensitive coatings were translucent with a smooth matte surface. Upon stepwise exposure for 1 to 10 minutes under a line negative to the light from three RS sunlamps at a distance of about 9 inches and subsequent development in 5% aqueous lead nitrate solution, there were obtained visible images in all areas with the exposed portions being bright yellow and the unexposed portions pale yellow. Additional plates given longer exposures up to 20 minutes and developed in either aqueous lead nitrate or cobalt nitrate solutions gave, respectively, yellow and brown images of higher contrast.

Example VIII

A mixture of 1.26 parts of n-dodecyl mercaptan, 1.1 parts (1.25 molar on mercaptan) of 1-decene, and 0.1 part of benzoin methyl ether was dispersed by means of a valve homogenizer in 75 parts of a 10% aqueous solu-

tion of medium viscosity (completely hydrolyzed grade) polyvinyl alcohol. The dispersion was coated on glass plates and allowed to dry. A translucent photosensitive film of moderately smooth surface was obtained. Upon stepwise exposure for 2 to 10 minutes under a line negative to the light from two BL–360 fluorescent lamps at a distance of 3 inches followed by development in either aqueous lead nitrate or cobalt nitrate solutions there were obtained, respectively, fair yellow and brown images at the 2 and 5 minute exposure levels.

Example IX

To 25 parts of a 10% solution of medium viscosity (completely hydrolyzed grade) polyvinyl alcohol in water were added a solution of 2 parts of potassium p-styrenesulfonate in 25 parts of water and a mixture of 1.26 parts (0.7 molar on sulfonate) of dodecyl mercaptan and 0.1 part of benzoin methyl ether. The mixture was passed through a valve homogenizer to disperse the thiol and initiator and the composition was then coated on glass plates and allowed to dry. The dry photosensitive coatings were very hazy with a matte surface. Upon stepwise exposure for 2, 5, and 10 minutes under a line negative to the light from three RS sunlamps at a distance of about nine inches, followed by development in an aqueous solution of lead nitrate for 15 minutes, with subsequent water rinsing and final drying, there was obtained in all portions a visible colored image of the text in the negative. Although the exposed areas were essentially free from color as in the other examples, most of the unexposed areas were also quite light in color. However, there was a dark yellow zone immediately adjacent to each exposed area giving an outline effect which markedly increased the visual contrast of the image.

Example X

Example VII was repeated using instead of styrene as the ethylenically unsaturated compound 3.36 parts (2.7 molar on mercaptan) of diallyl maleate. The coatings obtained were translucent with a smooth matte surface. Upon stepwise exposure ranging from 15 seconds to 16 minutes under a line positive to the light from three RS sunlamps at a distance of about 9 inches and subsequent development in aqueous cobalt nitrate solution, there was obtained a sharp red-colored image of the letter text of the positive in areas with exposure levels of less than 1 minute. In areas with longer exposures, the plate was obviously overexposed and portions of the image were missing.

Example XI

A mixture of 1.26 parts of n-dodecyl mercaptan, 1.06 parts (equimolar on mercaptan) of diethyl maleate, and 0.1 part of benzoin methyl ether was dispersed by means of a valve homogenizer in 50 parts of a 5% aqueous solution of medium viscosity (completely hydrolyzed grade) polyvinyl alcohol. In a similar manner, a dispersion of 1.26 parts of dodecyl mercaptan, 0.89 part (equimolar on mercaptan) of 1-decene, and 0.1 part of benzoin methyl ether in 50 parts of the polyvinyl alcohol solution was prepared. The two dispersions were combined, mixed thoroughly, coated on glass, and allowed to dry. Coatings obtained were very hazy and somewhat rough. Upon stepwise exposure for 2, 4, and 8 minutes under a line negative to the light from three RS sunlamps at a distance of about 9 inches and subsequent development with a 5% aqueous solution of cobalt nitrate hexahydrate, there was obtained a colorless visible image of the text on a faint pink background in all exposure steps.

Example XII

A mixture of 1.0 part of o-thiocresol, 1.13 parts (equimolar on thiocresol) of 1-decene, 0.1 part of benzoin methyl ether, and 7.0 parts of diethyl ether was dispersed by means of a valve homogenizer in 75.0 parts of a warm 5% solution of gelatin in water. The dispersion was cast on glass and allowed to gel and dry. The coatings obtained were translucent with a matte surface. Exposure for 5–50 minutes under a line negative to the light from three RS sunlamps at a distance of about 9 inches, followed by development in 5% aqueous lead nitrate solution, gave a good image of the text in all exposure steps. The image was colorless or light yellow on a dark yellow background. Complete reaction of the o-thiocresol so that the exposed portions were entirely colorless required an exposure of about 30 minutes. Development with 5% solutions of copper sulfate in water or mercurous nitrate in dilute nitric acid also gave images but of much lower contrast than those obtained with the lead nitrate solution. Similar results to those described above were obtained from coatings made by substituting 1.39 parts (equimolar on thiocresol) of diethyl maleate for the 1-decene in the above preparation.

Example XIII

To 25.0 parts of a 10% aqueous solution of a medium viscosity (completely hydrolyzed grade) polyvinyl alcohol there were added 20.0 parts of water and 0.5 part of glycerol followed by a mixture of 0.9 part of 2-mercaptoacetic acid, 0.75 part (1.1 molar on the acid) of acrylamide, 0.1 part of sodium 2-anthraquinonesulfonate, and 4.0 parts of ethanol. The solution was coated on glass plates and allowed to dry. The dry, photosensitive coating was clear and nontacky. Exposure for 5, 10, and 20 minutes under a line negative to the light from three RS sunlamps at a distance of about 9 inches followed by development in 5% aqueous lead nitrate solution gave a very faint image in all exposure steps. The exposed portions were clear while the unexposed areas were hazy white.

Example XIV

A solution of 0.91 part of dodecyl mercaptan, 0.87 part (0.78 molar based on mercaptan) of triallyl cyanurate, and 0.045 part of benzoin methyl ether was dispersed by means of a valve homogenizer in 75 parts of a warm 5% gelatin solution in water. The dispersion was coated on both glass plates and gelatin-subbed cellulose acetate film base and allowed to gel and dry. Translucent semi-matte coatings were obtained. Exposure of these coatings under a continuous tone negative for 10–30 minutes to the light from two 15-watt BL–360 fluorescent lamps at a distance of 3 inches, followed by development in 5% aqueous lead nitrate solution, resulted in a good yellow reproduction of the original negative. Gradation was excellent and comparable to that of the original at the longer exposure levels. A similar pink reproduction was obtained with aqueous cobalt nitrate solution of the developer.

The invention is generic to the use of one or more unsaturated compounds substantially homogeneously dispersed through the said protective colloid binder in combination with one or more thiols or mercaptans complementarily reactive therewith on irradiation with actinic light. The unsaturated compounds can be substituted or unsubstituted, the primary requirement being that they be stable and non-volatile in the dispersion at normal conditions of temperature and pressure and reactive with the thiol or mercaptan component upon irradiation with actinic light. The preferred ethylenically unsaturated compounds are monomers and contain ethylenic carbon-carbon bonds and are either liquids or form liquid compositions with the thiols. Suitable specific examples of these preferred unsaturated components include the wholly hydrocarbon branched and straight chain olefins, such as the heptenes, the octenes, and the like, including 3-ethyl-octadecene, 2,2-dimethyl-3-hexene, 2,4,4-trimethyl-1-pentene, 3-ethyl-2-pentene, and the like; the cycloaliphatic or alicyclic olefins, such as cyclohexene, methylcyclopentene, isopropenylcyclopropane, cycloheptene, 3-ethylcyclopentene, 3-n-propylcyclopentene, 1-ethyl-4-methylcyclohex-

ene, cyclohexylcyclohexene, and the like; the aryl-substituted wholly hydrocarbon olefins, such as styrene, allylbenzene, 1-phenyl-1-propene, m-allylethylbenzene, β-vinylnaphthalene, and the like. The preferred olefins will contain between 4 and 20 carbon atoms since olefins containing fewer carbon atoms are generally too low boiling to be liquid under the conditions required and olefins containing more than 20 carbon atoms are generally solid under the conditions required. It must be stressed that the olefin/mercaptan mixture must be liquid in intimate dispersion throughout the polymeric protective colloid binder.

The ethylenically unsaturated compounds which are useful in accordance with the invention are not limited to the monoolefinically unsaturated compounds, as polyolefinic compounds can be used. Suitable examples of these include the wholly aliphatic diolefin hydrocarbons, e.g., 1,2 - pentadiene, 1,4 - pentadiene, 1,2 - hexadiene, 4,5-dimethyl-2,6-octadiene; the cycloaliphatic, i.e., alicyclic, diolefinic hydrocarbons, such as cyclopentadiene, cyclohexadiene, 1-vinyl-1-cyclohexene, 1,3-butenyl-1-cyclohexene; aromatic-substituted diolefin hydrocarbons, e.g., 1-phenyl-1,2-butadiene, divinylbenzene, trivinylbenzene, and the like.

Because of greater reactivity particularly as a function of time, i.e., with shorter reaction times, the most outstanding of the preferred unsaturated components are those wherein the ethylenic C=C linkages are terminal, i.e., in the case of the olefins, the 1-olefins.

Suitable substituted unsaturated compounds include the vinyl carboxylates or precursors thereto, e.g., those wherein the vinyl group is in the acid portion of the molecule, such as acrylic acid and the esters and amides thereof, e.g., alkyl acrylates and methacrylates containing alkyl groups of 1 to 12 carbon atoms, methyl acrylate, ethyl acrylate, n-butyl acrylate and the corresponding methacrylates; acrylonitrile, acrylamide, methacrylonitrile; the α-alkylacrylic acids and esters and amides thereof, such as methacrylic acid and ethacrylic acid and esters and amides thereof such as methyl, n-propyl, n-butyl, isopropyl, and cyclohexyl meth- and eth-acrylates, and methacrylamide; α-substituted acrylic acids and esters thereof, such as ethyl α-chloroacrylate and ethyl α-cyanoacrylate; those vinyl components wherein the vinyl group is in the non-acid portion of the molecule, such as the vinyl esters, e.g., vinyl acetate, vinyl chloroacetate, vinyl trimethylacetate, vinyl propionate and vinyl benzoate; vinyl aryls, such as styrene; and vinylidene halides, such as vinylidene chloride. These ethylenically unsaturated compounds are capable of forming a high polymer in a short period of time by photoinitiated addition polymerization in the presence of an addition polymerization initiator therefor activatable by actinic light.

As is true of the unsaturated component, the mercaptan- or thiol-containing compound must either be liquid or form, together with the unsaturated compound, a liquid composition under the conditions normally encountered and must be complementarily reactive with the unsaturated component or components under irradiation by actinic light, alone or in the presence of a photosensitizer as described above. The mercaptan- or thiol-containing component also may be substituted or unsubstituted. Suitable additional examples of these include: aliphatic mercaptans, such as alkyl mercaptans of 2 to 18 carbon atoms, ethyl mercaptan, isopropyl mercaptan, butyl mercaptan, hexyl mercaptan; unsaturated mercaptans, e.g., allyl mercaptan; aromatic mercaptans, e.g., thiophenol, m-thiocresol and o-ethylthiophenol; araliphatic mercaptans, e.g., benzyl mercaptan and β-phenylethyl mercaptan; heterocylic mercaptans, e.g., α-furfuryl mercaptan and 2-mercaptomethyltetrahydrofuran. In the case of the unsaturated mercaptans, no second reactant is necessary, i.e., the unsaturated component, preferably the ethylenic C=C linkage, and the mercaptan component being present in the same molecule. Suitable specific functionally substituted mercaptans or thiol components include the halomercaptans, such as β-chloropropyl mercaptan, γ-bromopropyl mercaptan, o-iodothiophenol and m-trifluoromethylthiophenol; mercapto alcohols, ethers, and ketones, such as 2-methoxyethyl mercaptan, γ-hydroxypropyl mercaptan, β-ethoxyethyl mercaptan and 2-phenoxyethyl mercaptan; mercapto acids and esters, such as ethylmercaptoacetate, i.e., ethyl thioglycolate; mercapto amines, e.g., β-diethylaminoethyl mercaptan. Suitable specific examples of the di- and higher polythiol compounds which can be used include 1,2-ethanedithiol, trimethylene dimercaptan, heptamethylene dimercaptan, i.e., 1,3-propylenedithiol, and 1,7-heptamethylenedithiol.

In its development aspects the invention is generic to the use of one or more soluble salts of metals whose mercaptides are colored and insoluble. The salts can be used in any one of the oxidation states of the metal. Generally speaking, simple aqueous solutions of the salts will be used. Other additives can be used in the solutions, for instance, the lower aliphatic alcohols, where a synthetic polymeric binder is being used, to increase the penetration speed of the developer. Any of the soluble inorganic salts of the metals can be used, including the hydrohalide salts, i.e., the chlorides, bromides, and iodides; the nitrites, the nitrates, and the like. The soluble salts of the metal with organic acids can equally well be used, and in those instances where for reasons of increased penetration speed an organic additive is used in the developer, the organic salts will frequently be preferred. Included among the soluble organic salts are the acetates and propionates. Suitable specific examples of the salts which can be used include soluble salts of group I–B, e.g., silver nitrate; soluble salts of group II–B, e.g., zinc chloride, mercuric nitrate; soluble salts of groups III–B to VII–B, e.g., scandium nitrate, zirconium chloride, niobium acetate, chromium chloride, tungsten nitrate, manganese dichloride, rhenium bromide; and soluble salts of group VIII, such as ferric chloride, nickel acetate, cobalt bromide, and ruthenium nitrate. The preferred salts, due to the greater color intensity developed thereby, are the lead, silver, bismuth, and cobalt salts. In general, the development will be carried out at a temperature from 10 to 30° C. and for a period of 0.5 to 60 minutes. When relief images are made in accordance with the invention, the removal of the exposed, soluble portion of the layer can be aided by spraying and/or brushing such portions during the development. Such development will be carried out at a temperature from 40 to 60° C. and for a period of 30 to 300 seconds.

The nature of the image, i.e., as to the color thereof, will vary as a function of both the particular mercaptan and metal salt being used since the colors of the mercaptides formed similarly vary. In some instances, particularly in the case of the mercaptans containing a solubilizing functional group, e.g., a carboxyl group, all the metal salts will not give identical results since some of the mercaptides formed are soluble. These variations are illustrated in the following table so that a selection of the metal salt to be used as a developer can be made.

Metal Ion	n-Dodecyl Mercaptan, Color of Precipitate	o-Thiocresol, Color of Precipitate	2-Mercaptoacetic Acid, Color of Precipitate
Cu^{++}	white	light yellow	cream.
Ag^{+}	very light yellow	do	yellow.
Cd^{++}	white	white	clear solution.
Hg^{++}	do	gray	gray.
Hg^{++}	do	white	heavy white.
Pb^{++}	yellow	heavy yellow	white.
Be^{+++}	bright yellow	orange droplets (liquid).	yellow solution.
Fe^{++}	gray-yellow	yellow	clear solution.
Co^{++}	pink solution, white.	pink solution, white.	brown-red solution.
Ni^{++}	green-white	brown	clear solution.

In formulating the dispersions of the liquid olefin/mercaptan mixture in the polymeric binder, the techniques

well known and established in the art for the preparation of silver halide-based photographic emulsions will be used. As is common in the preparation of such emulsions or dispersions, many additives can and frequently will advantageously be used to control the size of the dispersion and/or the degree of flowability, ease of coatability, and the like, of the resultant emulsion. Among such additives are surface-active dispersing agents, e.g., those of U.S. 2,752,246, which are non-ionic surface-active dispersing agents containing at least 6 intralinear oxyalkylene groups of 2 to 3 carbon atoms linked through an atom taken from the group consisting of O, S, and N atoms to a hydrophobic groups, including a hydrocarbon group of at least 8 carbon atoms, containing an alkyl radical of at least 4 carbon atoms. The proportions of any such non-ionic dispersing agent used will generally range from 1–30% of the weight of the liquid olefin/mercaptan combination. Other conventional additives for facilitating the preparation of the dispersion can also be used.

The invention is likewise generic to the use of mixtures of the soluble metal developing salts, as well as mixtures of the olefins and mercaptan reactants. By suitable control of the relative concentration and identity of the soluble metal developing salts the color of the image thereby produced can likewise be controlled.

The invention is also generic to other methods of developing the desired color image. Thus, any chemical reaction involving either an unsaturated compound or a mercaptan which produces a colored insoluble reaction product can be used since the light reaction, i.e., in the exposed areas, removes both the unsaturated and the thiol-containing components; whereas, in the unexposed areas, both these components remain available for reaction. Suitable specific illustrations of the kind of reactions that can be used in addition to the formation of the colored insoluble mercaptides, include dye formation from the mercaptan component.

Still another specific developer solution for aliphatic mercaptans comprises a slightly alkaline solution of sodium nitroprusside, in which case the color image is a deep wine color. In those instances where an aromatic mercaptan is used, the same color image can be developed from nitroprusside, but the solution should be made alkaline with ammonium hydroxide rather than sodium hydroxide.

The image-bearing materials which can be used in conjunction with one of the elements of the present invention in the preparation of a color image or a relief positive by the process of this invention include both process transparencies, e.g., line and halftone transparencies, and continuous tone transparencies as well as semi-opaque copy materials including paper with drawings, type matter or typewritten matter thereon. Because of the greater color contrast obtained in the process of this invention when the process transparencies are used, the process will more generally be applied to the use of such materials, i.e., to the use of transparencies wherein the opaque areas are all of substantially the same optical density, which is generally quite high, and the transparent areas are all of substantially the same optical density, which is substantially zero.

The printing elements obtained as described above in one embodiment of this invention are useful in the preparation of planographic prints as well as imbibition prints and also in some instances in intaglio printing. The plates are obviously useful for multicolor printing.

An advantage of this invention is that it provides a new type of photographic material which is highly versatile and can be used for the direct formation of positive images. A further advantage is that the photographic material does ot require skilled operators or technicians for its use in forming direct positives. Another advantage is that the reproduction processes of the invention can be carried out quickly and do not require highly skilled operators. A further advantage is that a large number of reproductions can be made from any material to be copied. A still further advantage is that the photosensitive materials can be used for the production at the same time of either a direct positive or a positive duplicating matrix.

Still other advantages will be apparent to those skilled in the art.

I claim:

1. A photosensitive element for the formation of direct positive images comprising a support and a photosensitive layer comprising (1) a water-permeable, hydrophilic organic colloid binding agent having a molecular weight greater than 5,000, possessing protective colloid properties and forming thin solid films which are freely permeable to water, having dispersed therethrough (2) a thiol taken from the group consisting of saturated and unsaturated aliphatic mercaptans, aromatic mercaptans, araliphatic mercaptans, and heterocyclic mercaptans, said mercaptans being complementarily reactive with ethylenically unsaturated monomeric compounds upon irradiation with actinic light and forming colored insoluble mercaptides with silver nitrate and (3) a normally liquid ethylenically unsaturated monomeric compound of 4 to 20 carbon atoms and being reactive with said thiol upon irradiation with actinic light; said hydrophilic colloid being present in an amount from 35% to 85%, said thiol in an amount from 5% to 35% and said ethylenically unsaturated compound in an amount from 5% to 35%, all by weight, of said layer.

2. An element as set forth in claim 1 wherein said thiol is an alkyl mercaptan of 5 to 18 carbon atoms.

3. An element as set forth in claim 1 wherein said thiol is an aromatic mercaptan.

4. An element as set forth in claim 1 wherein said unsaturated compound is an olefin.

5. An element as set forth in claim 1 wherein said colloid is gelatin.

6. An element as set forth in claim 1 wherein said support is paper.

7. An element as set forth in claim 1 wherein said unsaturated compound is an alkyl ester of an acrylic acid wherein said alkyl group has 1 to 6 carbon atoms.

8. An element as set forth in claim 1 wherein said layer contains an addition polymerization initiator activatable by actinic light in an amount from 0.01 to 10.0% by weight of said layer.

9. A process for producing direct positive images which comprises (*a*) exposing to actinic light, imagewise, a photosensitive layer comprising (1) a water-permeable hydrophilic organic colloid binding agent having a molecular weight greater than 5,000, possessing protective colloid properties and forming thin solid films which are freely permeable to water, having dispersed therethrough (2) a thiol taken from the group consisting of saturated and unsaturated aliphatic mercaptans, aromatic mercaptans, araliphatic mercaptans, and heterocyclic mercaptans, said mercaptans being complementarily reactive with ethylenically unsaturated monomeric compounds upon irradiation with actinic light and forming colored insoluble mercaptides with silver nitrate and (3) a normally liquid ethylenically unsaturated monomeric compound of 4 to 20 carbon atoms and being reactive with said thiol upon irradiation with actinic light; said hydrophilic colloid being present in an amount from 35% to 85%, said thiol in an amount from 5% to 35% and said ethylenically unsaturated compound in an amount from 5% to 35%, all by weight, of said layer, and (*b*) developing the exposed layer by treating it with an aqueous solution having dissolved therein a metal salt the metal ion of which forms an insoluble product with said thiol, whereby a protective colored image is formed in the non-exposed areas of said photosensitive layer.

10. A process as set forth in claim 9 wherein said thiol is an alkyl mercaptan of 5 to 18 carbon atoms.

11. A process as set forth in claim 9 wherein said thiol is an aromatic mercaptan.

12. A process as set forth in claim 9 wherein said compound is an olefin.

13. A process as set forth in claim 9 wherein said colloid is gelatin.

14. A process as set forth in claim 9 wherein said support is paper.

15. A process as set forth in claim 9 wherein said unsaturated compound is an alkyl ester of an acrylic acid wherein the alkyl group contains from 1 to 6 carbon atoms.

16. A process as set forth in claim 9 wherein said

layer contains an addition polymerization initiator activatable by actinic light in an amount from 0.01 to 10.0% by weight of said layer.

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