United States Patent Office

3,623,879
Patented Nov. 30, 1971

3,623,879
PROCESS OF FORMING A CONTINUOUS TONE PHOTOGRAPHIC IMAGE

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No Drawing. Filed Oct. 11, 1968, Ser. No. 766,948
Int. Cl. G03c *1/68*
U.S. Cl. 96—115 21 Claims

ABSTRACT OF THE DISCLOSURE

This invention is directed toward forming a silverless continuous tone photographic image having a scale index between 0.5 and 1.5 and a gamma of 0.5–1.5 (see "Kodak Notes on Practical Densitometry," Pamphlet No. E59, pp. 1–17, Eastman Kodak Co., Rochester, N.Y., for definitions), from a supported pigment or dye filled liquid photosensitive composition consisting essentially of a polyene containing at least two reactive unsaturated carbon to carbon bonds per molecule, a photosensitizer and a pigment or dye by selectively insolublizing portions of the composition on exposure to actinic radiation and removing the unexposed liquid portion of the composition from the support.

Continuous tone photographic materials used today consist of silver halide emulsions coated on supports, the silver halide being converted to metallic silver by the action of light and a developer. The system has several disadvantages. One disadvantage is the skyrocketing cost of silver due to silver being in such short supply. Another drawback is that all work must be done in the dark, thus necessitating costly darkrooms. Our materials do not employ silver and do not require expensive, inconvenient darkrooms as they are sensitive only to U.V. light. Also, conventional photographic printing materials are coated on paper since the support has to be permeable to the aqueous solution of developer. In our process the image is formed on a transparent support that can then be laminated to any kind of backing—cloth, wood, plastic, metal, etc. to give a wide variety of effects.

Recently Du Pont has marketed "Crolux," a photopolymerizable composition that yields images on exposure to light. Crolux, however, gives only black and white images and no intermediate gray tones and thus is not adaptable to use as a photographic print medium.

One object of this invention is to prepare a material giving a continuous tone photographic image having a scale index between 0.5 and 1.5 and a gamma of 0.5–1.5.

Another object of the instant invention is to prepare such material without use of silver.

A third object is to prepare such a material that can be processed in normal room lighting.

Yet another object of the present invention is to prepare a photographic film and print material giving an image quality superior to any known non-silver system.

Another object is to prepare printing materials having different contrast ranges so that they will give good prints from both "hard" and "soft" negatives.

Still another object of the invention is to provide a new, simple technique for preparing color prints from color separation negatives.

A further object is to provide a means of producing large continuous tone transparencies for use in overhead projectors.

A still further object of the invention is to provide a low cost simple means of reproducing microfilm.

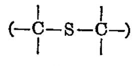
Summarily, it has been found that photographic images can be prepared by sandwiching a layer adjusted to a uniform thickness in the range 0.3–50 mils of a pigment or dye filled liquid photosensitive composition having a viscosity in the range 0 to 20 million centipoises at 70° C. and a photosensitizer or curing rate accelerator between two films at least one of which transmits actinic radiation, exposing said composition to actinic radiation through an image-bearing, continuous tone transparency maintained adjacent to and preferably in contact with the transparent support film of the laminates and substantially parallel to the layer of said composition whereby portions of the composition exposed to actinic radiation on the transparent support film proximate the actinic radiation source react to become solidified to form an image and portions of said composition on the opposite film away from the actinic radiation source, react to become solidified to form a reverse image, separating said films and removing the unpolymerized liquid photosensitive composition therefrom thus forming a continuous tone positive and negative image, said positive image being laminated to a background material, e.g. a high reflectance material, such as white pigmented polyvinyl chloride to give a continuous tone photographic print.

As used herein the term "liquid photosensitive composition" means a liquid composition having a viscosity in the range 0 to 20 million centipoises at 70° C. which is solidified either by photocuring or photopolymerization or both on exposure to actinic light.

One photosensitive system which is suitable for use in the instant invention is that set out in a copending application having U.S. Ser. No. 674,773 filed Oct. 12, 1967 assigned to the same assignee and incorporated by reference herein. In said system a printing plate is formed from a layer of a U.V. photocurable composition consisting of a 2 to 98 parts by weight of a polyene containing at least two unsaturated carbon to carbon bonds per molecule, 98 to 2 parts by weight of a polythiol containing two or more thiol groups per molecule and a photocuring rate accelerator, i.e., a photosensitizer, e.g. benzophenone, said layer preferably being adhered to a support.

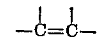
As used therein polyenes and polyyne refer to a simple or complex species of alkenes or alkynes having a multiplicity, i.e., at least 2, "reactive" carbon to carbon unsaturated functional groups per average molecule. For example, a diene is a polyene that has two "reactive" carbon to carbon double bonds per average molecule, while a diyne is a polyyne that contains in its structure two "reactive" carbon to carbon triple bonds per average molecule. Combinations of "reactive" double bonds and "reactive" triple bonds within the same molecule are also operable. An example of this is monovinylacetylene, which is a polyeneyne under our definition. For purposes of brevity all these classes of compounds will be referred to herein as polyenes.

As used herein the term "reactive" unsaturated carbon to carbon groups means groups which will react under proper conditions as set forth herein with thiol groups to yield the thioether linkage



$$(-\overset{|}{\underset{|}{C}}-S-\overset{|}{\underset{|}{C}}-)$$

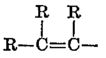
as contrasted to the term "unreactive" carbon to carbon unsaturation which means



$$-\overset{|}{C}=\overset{|}{C}-$$

groups when found in aromatic nucleii (cyclic structures exemplified by benzene, pyridine, anthracene, tropolone and the like) which do not under the same conditions react with thiols to give thioether linkages. In the instant invention, products from the reaction of polyenes with polythiols which contain 2 or more thiol groups per average molecule are called polythioether polymers or polythioethers.

One group of polyenes operable in the instant invention to react with polythiols to form a photographic medium is that taught in a copending application having Ser. No. 617,801 filed Feb. 23, 1967, and now abandoned, assigned to the same assignee and incorporated herein by reference. This group includes those having a molecular weight in the range 50 to 20,000, a viscosity ranging from 0 to 20 million centipoises at 70° C. of the general formula: $[A]-(X)_m$ wherein X is a member of the group consisting of

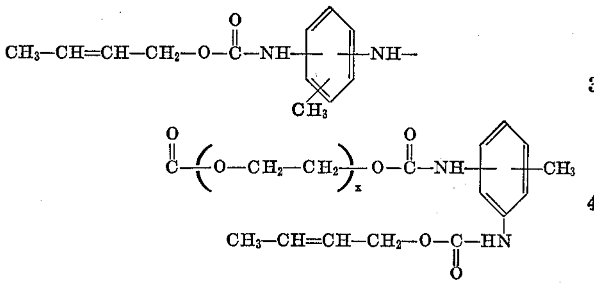


$$R-\overset{R}{C}=\overset{R}{C}-$$

and R—C≡C—; *m* is at least 2; R is independently selected from the group consisting of hydrogen, halogen, aryl, substituted aryl, cycloalkyl, substituted cycloalkyl, aralkyl, substituted aralkyl and alkyl and substituted alkyl groups containing 1 to 16 carbon atoms and A is a polyvalent organic moiety free of (1) reactive carbon to carbon unsaturation and (2) unsaturated groups in conjugation with the reactive ene or yne groups in X. Thus A may contain cyclic groupings and minor amounts of hereto atoms such as N, S. P or O but contains primarily carbon-carbon, carbon-oxygen or silicon-oxygen chain linkages without any reactive carbon to carbon unsaturation.

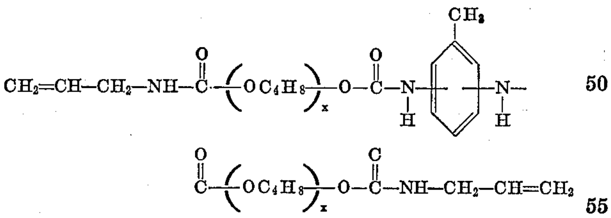
Examples of operable polyenes from this group include but are not limited to

(1) crotyl-terminated polyurethanes which contain two "reactive" double bonds per average molecule in a rear terminal position of the average general formula:



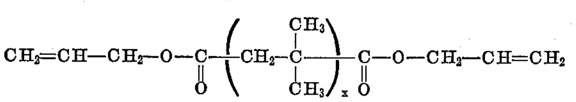
wherein *x* is at least 1,

(2) the following structure which contains terminal "reactive" double bonds:



where *x* is at least 1,

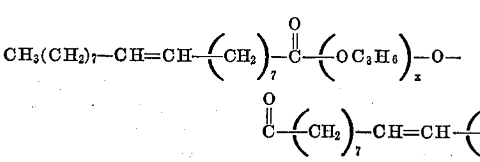
(3) the following structure which contains terminal "reactive" double bonds:



$$CH_2=CH-CH_2-O-\underset{\|}{\overset{}{C}}\!\!\left(CH_2-\overset{CH_3}{\underset{CH_3}{C}}\right)_{x}\!\!-\underset{O}{\overset{}{C}}-O-CH_2-CH=CH_2$$

where *x* is at least 1, and

(4) the following structure which contains near terminal "reactive" double bonds:

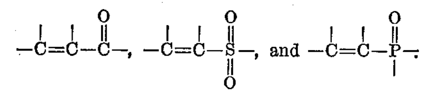


$$CH_3(CH_2)_7-CH=CH-(CH_2)_7-\overset{O}{\overset{\|}{C}}-(OC_3H_6)_x-O-\overset{O}{\overset{\|}{C}}-(CH_2)_7-CH=CH-(CH_2)_7CH_3$$

where *x* is at least 1.

A second group of polyenes operable in the instant invention includes unsaturated polymers in which the double or triple bonds occur primarily within the main chain of the molecules. Examples include conventional elastomers (derived primarily from standard diene monomers) such as polyisoprene, polybutadiene, styrene-butadiene rubber, isobutylene-isoprene rubber, polychloroprene, styrene-butadiene-acrylonitrile rubber and the like; unsaturated polyesters, polyamides, and polyurethanes derived from monomers containing "reactive" unsaturation, e.g. adipic acid-butenediol, 1,6-hexanediamine-fumaric acid and 2,4-tolylene diisocyanate-butenediol condensation polymers and the like.

A third group of polyenes operable in this invention includes those polyenes in which the reactive unsaturated carbon to carbon bonds are conjugated with adjacent unsaturated groupings. Examples of operable reactive conjugated ene systems include, but are not limited to, the following:



$$-\overset{|}{C}=\overset{|}{C}-\overset{O}{\overset{\|}{C}}-,\quad -\overset{|}{C}=\overset{|}{C}-\underset{O}{\overset{O}{S}}-,\ \text{and}\ -\overset{|}{C}=\overset{|}{C}-\underset{|}{\overset{O}{P}}-$$

A few typical examples of polymeric polyenes which contain conjugated reactive double bond groupings such as those described above are polyethyleneether glycol diacrylate having a molecular weight of about 750, polytetramethyleneether glycol dimethacrylate having a molecular weight of about 1175, the triacrylate of the reaction product of trimethylolpropane with 20 moles of ethylene oxide, and the like.

Included in the term "polyenes" as used herein are those materials which in the presence of an inert solvent, aqueous dispersion or plasticizer fall within the visocity range set out above at 70° C.

As used herein, the term polythiols refers to simple or complex organic compounds having a multiplicity, i.e. at least 2, of pendant or terminally positioned —SH functional groups per average molecule.

On the average the polythiols must contain 2 or more —SH groups/molecule. They usually have a viscosity range of 0 to 20 million centipoises (cps.) at 70° C. as measured by a Brookfield viscometer. Included in the term "polythiols" as used herein are those materials which in the presence of an inert solvent, aqueous dispersion or plasticizer fall within the viscosity range set out above at 70° C. Operable polythiols in the instant invention usually have molecular weights in the range 50–20,000, preferably 100–10,000.

The polythiols operable in the instant invention can be exemplified by the general formula: $R_8-(SH)_n$ where *n* is at least 2 and R_8 is a polyvalent organic moiety free from "reactive" carbon to carbon unsaturation. Thus R_8 may contain cyclic groupings and minor amounts of hetero atoms such as N, S, P or O but primarily contains carbon-hydrogen, carbon-oxygen, or silicon-oxygen containing chain linkages free of any "reactive" carbon to carbon hydrogen, carbon-oxygen, or silicon-oxygen containing chain linkages free of any "reactive" carbon to carbon unsaturation.

One class of polythiols operable with polyenes in the instant invention to obtain an essentially odorless cured polythioether photographic medium are esters of thiol-containing acids of the general formula:

$$HS-R_9-COOH$$

where R_9 is an organic moiety containing no "reactive" carbon to carbon unsaturation with polyhydroxy compounds of the general structure: $R_{10}-(OH)_n$ where R_{10} is an organic moiety containing no "reactive" carbon to carbon unsaturation and *n* is 2 or greater. These components will react under suitable conditions to give a polythiol having the general structure:

$$R_{10}-\left(O\overset{O}{\overset{\|}{C}}-R_9-SH\right)_n$$

where R_9 and R_{10} are organic moieties containing no "reactive" carbon to carbon unsaturation and n is 2 or greater.

Certain polythiols such as the aliphatic monomeric polythiols (ethane dithiol, hexamethylene dithiol, decamethylene dithiol, tolylene-2,4-dithiol, etc.) and some polymeric polythiols such as a thiol-terminated ethylcyclohexyl dimercaptan polymer, etc. and similar polythiols which are conveniently and ordinarily synthesized on a commercial basis although having obnoxious odors, are operable in this invention. Examples of the polythiol compounds preferred for this invention because of their relatively low odor level and fast curing rate include but are not limited to esters of thioglycolic acid

$$(HS—CH_2COOH)$$

α-mercaptopropionic acid ($HS—CH(CH)_3—COOH$) and β-mercaptopropionic acid ($HS—CH_2CH_2COOH$) with polyhydroxy compounds such as glycols, triols, tetraols, pentaols, hexaols, etc. Specific examples of the preferred polythiols include but are not limited to ethylene glycol bis (thio glycolate), ethylene glycol bis (β-mercaptopropionate), trimethylolpropane tris (thioglycolate), trimethylolpropane tris (β-mercaptopropionate), pentaerythritol tetrakis (thioglycolate) and pentaerythritol tetrakis (β-mercaptopropionate), all of which are commercially available. A specific example of a preferred polymeric polythiol is polypropylene ether glycol bis(β-mercaptopropionate) which is prepared from polypropylene-ether glycol (e.g. Pluracol P2010, Wyandotte Chemical Corp.) and β-mercaptopropionic acid by esterification.

The preferred polythiol compounds are characterized by a low level of mercaptan-like odor initially, and after reaction, give essentially odorless cured polythioether end products which are commercially useful resins or elastomers for a photographic medium.

As used herein the term "odorless" means the substantial absence of the well-known offensive and sometimes obnoxious odors that are characteristic of hydrogen sulfide and the derivative family of compounds known as mercaptans.

The term "functionality" as used herein refers to the average number of ene or thiol groups per molecule in the polyene or polythiol, respectively. For example, a triene is a polyene with an average of three "reactive" carbon to carbon unsaturated groups per molecule and thus has a functionality (f) of three. A dithiol is a polythiol with an average of two thiol groups per molecule and thus has a functionality (f) of two.

It is further understood and implied in the above definitions that in these systems, the functionality of the polyene and the polythiol component is commonly expressed in whole numbers although in practice the actual functionality may be fractional. For example, a polyene component having a nominal functionality of 2 (from theoretical considerations alone) may in fact have an effective functionality of somewhat less than 2. In an attempted synthesis of a diene from a glycol in which the reaction proceeds to 100% of the theoretical value for complete reaction, the functionality (assuming 100% pure starting materials) would be 2.0. If, however, the reaction were carried to only 95% of theory for complete reaction, about 10% of the molecules present would have only one ene functional group, and there may be a trace of material that would have no ene functional groups at all. Approximately 90% of the molecules, however, would have the desired diene structure and the product as a whole then would have an actual functionality of 1.9. Such a product is useful in the instant invention and is referred to herein as having a functionality of 2.

The aforesaid polyenes and polythiols can, if desired, be formed or generated in situ and still fall within the scope of the instant invention.

To obtain the maximum strength, solvent resistance, creep resistance, heat resistance and freedom from tackiness, the reaction components consisting of the polyenes and polythiols of this invention are formulated in such a manner as to give solid, crosslinked, three dimensional network polythioether polymer systems on curing. In order to achieve such infinite network formation, the individual polyenes and polythiols must each have a functionality of at least 2 and the sum of the functionalities of the polyene and polythiol components must always be greater than 4. Blends and mixtures of the polyenes and the polythiols containing said functionality are also operable herein.

In general, it is preferred, especially at or near the operable lower limits of functionality in the polyene and polythiol, to use the polythiol and the polyene compounds in such amounts that there is one thiol group present for each ene group, it being understood that the total functionality of the system must be greater than four, and the functionality of the thiol and the diene must each be at least two. For example, if two moles of a triene are used, and a dithiol is used as the curing agent, making the total functionality have a value of five, it is preferable to use three moles of the dithiol. If much less than this amount of the thiol is used, the curing rate will be lower and the product will be weaker in some respects because of the reduced crosslink density. If much more than the stoichiometric amount of the thiol is used, the rate of cure may be higher, if that is desirable, although excessive amounts can lead to a plasticized crosslinked product which may not have the desired properties. However, it is within the scope of this invention to adjust the relative amounts of polyenes and polythiols to any values above the minimum scope disclosed herein which give desirable properties to the crosslinked polythioether. It must be emphasized that regardless of the ratio of polythiol to polyene, the total functionality of the system must be greater than four, or a crosslinked network will not result, and the product will be a swellable, chain-extended composition which is unsuitable for the purpose of this invention. Thus in practicing the instant invention to obtain a solid crosslinked photographic medium, it is necessary to use a polyene containing at least 2 unsaturated carbon to carbon bonds per molecule in an amount that the combined functionality of the unsaturated carbon to carbon bonds per molecule of polyene and the thiol groups per molecule of polythiol is greater than 4.

The above systems are preferred. However, any system having an initial viscosity in the range 0–20 million centipoises at 70° C. which can be filled with pigment or dye and then either photopolymerized, photocured or both to a solid polymer from which the unpolymerized material may be stripped by washing or other means is operable.

In the case of polyenes which are to be photopolymerized, it is preferable not to have a polythiol present in the composition, but rather to have only the ene monomer (usually a conjugated ene monomer which is commonly known as an addition polymerizable vinyl monomer) and a photoinitiator as the reactive components of the photopolymerizable composition. See U.S. 2,760,863; 3,380,831, etc. for examples of some of these kinds of systems.

The liquid photosensitive compositions to be converted to solid photographic material, in accord with the present invention may, if desired, include such additives as antioxidants, accelerators, dyes, inhibitors, activators, fillers, pigments, antistatic agents, flame-retardants agents, thickeners, thixotropic agents, surface-active agents, light scattering agents, viscosity modifiers, extending oils, plasticizers, tackifiers and the like within the scope of this invention. Such additives are usually preblended with the monomer or compound to be photosensitized or with the polyene or polythiol prior to or during the compounding step. Such fillers, however, unless they are used for the purpose of pigmenting or dying the image, should not be substantially opaque when present in the photosensitizable polymer. The aforesaid additives may be present in quantities up to 500 parts or more per 100 parts of the liquid photosensitive composition by weight and preferably 0.005–300 parts on the same basis, but each additive must be present in an amount which will not interfere with or inhibit the necessary photocuring or photopolymerization image-producing reaction or other required steps in the photographic process.

The colors of the continuous tone prints obtained by the practice of the instant invention can be of infinite variety. For example, if one desired a red and yellow print, a red pigment is included in the photosensitive composition and the resultant photosensitized image is laminated to a piece of high reflectance yellow paper to give a silverless, red and yellow continuous tone photographic print. By the same token, a yellow pigment can be employed and the photosensitized image can be laminated to a piece of high reflectance red paper.

For black and white prints, carbon blacks conventionally used for inks, plastics, rubbers, etc. may be employed as pigments. These include the so-called channel, furnace and thermal blacks having particle diameters of 5–250 millimicrons. Black dyes which are generally azine and azo organic compounds are also operable.

For colored prints any suitably colored dye is operable that does not contain groups which would inhibit the polymerization or curing system used.

The support to which the photosensitive composition is adhered can be formed from various materials such as plastic, glass, quartz and the like. The support is preferably a plastic having the characteristics of being flexible, adherable to the photosensitive composition on exposure to U.V. radiation or by other means and can transmit a substantial amount of U.V. light. The thickness of the support is dependent on its relative strength and dimensional stability to hold a specified thickness of the photosensitive composition and can be empirically determined by one skilled in the art. For example when an oriented polyethylene terephthalate in film form sold under the trade name Mylar is employed as the support, the Mylar film will usually have a thickness of about 0.5 to 10 mils.

The photosensitive reaction can be initiated by actinic radiation from sunlight or from special light sources which emit significant amounts of actinic light suitably in the wavelength range of 2200–4000 A. Thus, it is possible merely to expose the liquid photosensitive composition through the transparent support film to actinic radiation preferably in the range 2200–4000 A. under ambient conditions or otherwise and obtain a solid elastomeric or resinous product useful as a photographic material after development.

The photosensitive reaction rate can be increased by the use of a photosensitizer. As used herein a photosensitizer means either a photoinitiator as employed in a polymerization reaction or a curing rate accelerator as used in a curing reaction or both. For example benzophenone when added to a liquid photopolymerizable composition such as monomeric pentaerythritol triacrylate would be a photoinitiator whereas benzophenone would be a curing rate accelerator for the liquid photocurable composition comprised of a polyene and a polythiol.

Various photosensitizers are operable and well known to those skilled in the art. Exampes of photosensitizers include, but are not limited to, benzophenone, acetophenone, acenaphthene-quinone, methyl ethyl ketone, valerophenone, hexanophenone, γ-phenylbutyrophenone, p-morpholinopropiophenone, dibenzosuberone, 4-morpholinobenzophenone, 4′ - morpholinodeoxybenzoin, p-diacetylbenzene, 4-aminobenzophenone, 4′-methoxyacetophenone, benzaldehyde, α-tetralone, 9-acetylphenanthrene, 2-acetylphenanthrene, 10 - thioxanthenone, 3 - acetylphenanthrene, 3-acetylindole, 9-fluorenone, 1-indanone, 1,3,5-triacetylbenzene, thioxanthen-9-one, xanthene-9-one, 7-H-benz[de]anthracen-7-one, 1-naphthaldehyde, 4,4′ - bis(dimethylamino) benzophenone, fluorene-9-one, 1′-acetonaphthone, 2′-acetonaphthone and 2,3-butanedione, etc. which serve to give greatly reduced exposure times and thereby when used in conjunction with various forms of energetic radiation yield very rapid, commercially practical time cycles by the practice of the instant invention. The photosensitizers, i.e. curing rate accelerators or photoinitiators are usually added in an amount ranging from 0.0005 to 50% by weight, preferably 0.5 to 25%, of the photocurable or photopolymerizable composition in the instant invention. Such photosensitizers are also useful in that they control the contrast or gamma of the resulting image so that at low concentrations high contrast is obtained while at high concentrations low contrast is obtained. Hence photographic printing materials can be prepared that are equivalent to the "grades" of silver-based printing papers and can be matched to negatives of varying contrast.

The compounding of the components of the liquid photosensitive composition prior to exposure to U.V. radiation can be carried out in several ways. For example, in the case of the liquid photocurable composition, the polyene, the polythiol and any other additives, e.g. photosensitizer pigment or dye, are admixed in an inert atmosphere and charged to an aerosol can, drum, tube, or cartridge for subsequent use. Exposure of said admixed components to actinic radiation under ambient or elevated temperature conditions will initiate photocuring.

Another useful method of compounding the photocurable composition is to prepare by conventional mixing techniques but in the absence of actinic radiation a composition consisting of polyene, antioxidant (to inhibit spontaneous oxygen-initiated curing), polythiol, pigment, U.V. sensitizer or photoinitiator, and other inert additives. This composition generally can be stored in closed containers in the dark for extended periods of time, but on exposure to actinic radiation (e.g., ultraviolet light, sunlight, etc.) will cure controllably and in a very short time period to solid polythioether photographic products.

Conventional curing inhibitors or retarders operable with the photocurable compositions in the instant invention include but are not limited to hydroquinone; p-tert-butyl catechol; 2,6-ditert-butyl-p-methylphenol; phenothiazine and N-phenyl-2-naphthylamine.

The molecular weight of the polyenes of the instant invention can be measured by various conventional methods including solution viscosity, osmotic pressure and gel permeation chromatography. Additionally, the molecular weight can be sometimes calculated from the known molecular weight of the reactants.

The viscosity of the polyenes and polythiols was measured on a Brookfield viscometer at 30 or 70° C. in accord with the instructions therefor.

The thickness of the photosensitive composition layer that is converted to solid polymer is proportional to the intensity of the light that strikes it. Consequently, when exposed under a continuous tone negative, clear areas in the negative will correspond to thick areas of polymer, very dense areas in the negative to substantially no polymer and intermediate densities to intermediate thicknesses of polymer. The inverse correspondence between the density of the negative and the thickness (and hence opacity) of the filled photosensitive polymer results in the conversion of a continuous tone negative to a continuous tone print. Likewise, if the material is used in a camera, a continuous tone scene will be rendered as a continuous tone negative. Continuous tone separation negatives will likewise yield continuous tone transparencies from polymer films dyed with the complementary colors to the filters used to prepare the negatives. When these are superimposed, a continuous tone, full color print results.

The photosensitive material can be exposed to U.V. through a negative that is in contact with the support, or the negative image can be projected onto the support or the material can be placed in a camera with the support towards the lens and exposed like a conventional photographic film. The photosensitive polymer layer can be sandwiched between the transparent support and another film layer of various compositions, e.g. metal, paper, plastic etc. in which case the laminate can easily be handled in conventional photographic equipment such as cameras, enlargers, contact printing frames, etc. However, exposure can be made without this additional film layer by keeping the support level, e.g., with the photopolymer on top, and exposing to U.V. through the support from underneath the support. The development of the exposed film is carried out by immersing it in an aqueous solution containing a soap or detergent or a solvent, preferably alcohol and depending on the soap or detergent or solvent, is etched for periods ranging from 5 seconds up to one hour or more followed by blotting with a sponge and drying by a current of air or by radiant heat. However, for some of the photosensitive compositions the resulting image contains minor imperfections even when etched for extended periods in conjunction with mechanical means. It has now been found that using an aqueous solution of detergent or soap or a solvent in combination with ultrasonic activation of the bath to impart cavitation thereto, the etching time can be reduced to periods of 1 second to 10 minutes without enlisting mechanical aids such as brushes, sponges, etc. and the image obtained is far superior in quality and in fidelity of image reproduction to that previously obtained using photopolymerizable or photocurable materials and as good as that obtained using silver films.

The greater the difference in solubility between the solidified areas in the photosensitized plate and portions of said plate which remain liquid, the greater the efficiency of the process to make the image. Thus, it is important in the instant invention to select the right detergent, soap or solvent in the etching bath to facilitate removal.

A convenient method of carrying out the process of this invention is to place an image bearing positive or negative continuous tone transparency in a contact frame or enlarger parallel to the surface of a layer of a pigment or dye filled photosensitive composition, i.e. photocurable or photopolymerizable composition or both which has been cast directly on a transparent support and adjusted for uniformity of height by suitable means, e.g. a drawbar, precast mold and the like. The layer of the photosensitive composition can be covered with a film layer to form a sandwich, if desired. The layer of the photosensitive composition is exposed through the transparency and the transparent support to a source of actinic light suitably in the wavelength range of 2200–4000 A. until the layer is cured or polymerized or both to an insoluble stage in the exposed areas.

If the photosensitive composition is sandwiched between the transparent support layer and another layer, then the two layers are pulled apart leaving, on the transparent support, a cured reverse image of the transparency and uncured polymer. The transparent support bearing the reverse image is then developed by removing uncured polymer with an appropriate solvent. The photographic transparency is thereafter dried in air or in an oven at elevated temperatures up to about 150° C. Furthermore, if desired, the thus formed image can be further subjected to U.V. radiation for periods up to 10 minutes to further harden it.

The resulting image on its transparent support or backing may be further processed in a number of ways:

(1) If it is a negative made in a camera it may be used directly to make prints by any conventional process or by the process described in Example 10 below.

(2) If the transparency is a positive, it may be coated with any transparent adhesive or with a transparent photosensitive polymer laid down upon any white reflecting material to give a black and white print and reexposed to U.V. radiation for adhesion. Ordinary transparent adhesives are also operable and do not require U.V. reexposure. Color prints of three or more separation positives can be made in the same manner. Various tones may be obtained by varying the color cast of the support. Preferred backings are paper, white vinyl and any other white pigmented plastic.

(3) If a transparency for projection is desired, the image can be projected as is but preferably is laminated to another sheet of clear, transparent plastic to prevent possible handling damage to the image material.

The following examples will aid in explainign, but should not be deemed as limiting, the instant invention. In all cases unless otherwise noted, all parts and percentages are by weight.

EXAMPLE 1

Formation of polyene polymer

To a 2 liter flask equipped with stirrer, thermometer and gas inlet and outlet was charged 450 g. (0.45 moles) of polytetramethylene ether glycol, having a hydroxyl number of 112 and a molecular weight of approximately 1,000, along with 900 g. (0.45 moles) of polytetramethylene ether glycol having a hydroxyl number of 56 and a molecular weight of about 2,000, both commercially available from Quaker Oats Co. The flask was heated to 110° C. under vacuum and nitrogen and maintained thereat for 1 hour. The flask was then cooled to approximately 70° C. whereat 0.1 g. of dibutyl tin dilaurate was added to the flask. A mixture of 78 g. (0.45 moles) of tolylene diisocyanate and 78 g. (0.92 moles) of allyl isocyanate was thereafter added to the flask dropwise with continuous stirring. The reaction was maintained at 70° C. for 1 hour after addition of all the reactants. The thus formed allyl terminated polymer will hereinafter be referred to as Polymer A.

EXAMPLE 2

10 g. of Polymer A, 0.9 g. of pentaerythritol tetrakis (β-mercaptopropionate) and 1.5 g. carbon black (Sterling FT) in ethylene glycol monoethyl ether were mixed together and then heated in a vacuum oven for 5 minutes at 120° C. 0.15 g. of benzophenone was then added and mixed for 2 minutes. A 1 mil film of this material was spread on a sheet of opaque Mylar and a 1.0 mil thick sheet of clear Mylar rolled on top to produce a sandwich. The sandwich (clear side up) was exposed under a continuous tone photographic negative to a 275 watt U.V. lamp 9″ away for 3 minutes. Upon peeling the sandwich apart, a negative image, i.e. one identical to the photographic negative through which the light passed, adhered to the opaque Mylar and a positive continuous tone image, i.e. reversed relative to the negative through which the light passed was formed on the clear Mylar. Uncured polymer was removed from both the positive and negative images by blotting with paper soaked in ethanol. The positive image was then dried and laminated to a piece of high reflectance white paper to give a silverless, black and white continuous tone photographic print. The visual apperance and quality of the photocured polymer print obtained in the above manner was such that it could not be differentiated from a standard silver halide print made from the same negative using conventional printing technology.

EXAMPLE 3

The procedure and reactants of Example 2 were employed except that the sandwich was exposed under a 8000 watt Ascorlux pulsed xenon arc printing lamp and the images were cleaned by immersing in an ultrasonic bath containing ethanol at 60° C. for 10 seconds. The resulting positive image was dried and further cured by reexposure to the U.V. source for 5 minutes, followed by lamination to white pigmented polyvinylchloride with "Quik Stick," a commercial spray adhesive, to give a silverless, black and white, continuous tone photographic print.

EXAMPLE 4

The procedure and reactants of Example 3 were employed except that the clear sheet was oriented polystyrene instead of clear Mylar.

EXAMPLE 5

The procedure and reactants of Example 4 were employed except that a polycarbonate film was used for the clear sheet.

EXAMPLE 6

The procedure and reactants of Example 3 were employed except that Sterling FT carbon black was replaced by 1.0 g. of a black dye, i.e. Aquaprint 05–5207 Black K from Interchemical Co.

EXAMPLE 7

The procedure and reactants of Example 3 were employed except that 4.3% benzophenone based on the weight of photosensitive composition was used and the exposure time was 1 minute. A lower contrast print was obtained.

EXAMPLE 8

The procedure and reactants of Example 3 were employed except that 15% benzophenone based on the weight of photosensitive composition was used and a 0.2 minute exposure was employed. A very low contrast print was obtained.

EXAMPLE 9

A Kodak calibrated 21 step density wedge was exposed using the material of Example 7. The resulting image was used to generate a characteristic curve using a Kodak Densitometer. 16 steps were measured, the density of which, when plotted vs. log exposure gave a gamma of 1.2. This is equivalent to a medium speed silver emulsion film such as Panatomic X developed in a fine grain developer.

EXAMPLE 10

A sandwich of the photosensitive material of Example 8 was cut to 5″ x 4″ and the edges sealed by brief exposure to U.V. light. The "film" so obtained was loaded into Graphic cut film holders, transparent side nearest the lens. Exposures were made in a Polaroid MP 4 Technical camera fitted with a Goerz Dagor lens. Illumination of the subject (a watch lying on a 3 color picture as background) was supplied by two 275 watt sun lamps.

Exposures were 10–15 minutes at *f*4.5. A measurement of ASA rating for this film was made by measuring, with an exposure meter, what the exposure would have been with an ASA 100 film and then extrapolating back from the actual exposure. The ASA rating calculated in this way was 0.01.

The silverless photographic negative obtained as above was printed to give an excellent continuous tone silverless, black and white print using the procedure of Example 3. This example illustrates the formation of a photographic print in which the entire operation is carried out without the use of silver halide technology.

EXAMPLE 11

Using conventional silver halide film, three separation negatives were prepared by photographing a scene with a National One-Shot Camera. The negatives were prepared through the following filters: Wratten #25 (red), Wratten #58 (green) and Wratten #47 (blue).

The negative prepared through the red filter was printed using the procedure of Example 3 except that carbon black was replaced by 3.5 g. of Adpro blue dye.

The negative prepared through the green filter was printed using the procedure of Example 3 except that carbon black was replaced by 3.5 g. of Adpro yellow dye.

The negative prepared through the blue filter was printed using the procedure of Example 3 except that carbon black was replaced by 3.5 g. of Adpro red dye.

The three colored images were then superimposed and laminated to a white vinyl base to give an excellent silverless photographic three color print.

EXAMPLE 12

The reactants and procedures of Example 11 were used except that the three colored images were then superimposed and laminated to a piece of clear Mylar to give a three color transparency.

EXAMPLE 13

Example 2 was repeated except that Polymer A was replaced by 10 g. of a poly (1,3-butadiene) of approximately 2000 molecular weight and benzene was used as the washing solvent instead of ethanol. The results were essentially the same.

EXAMPLE 14

The procedure of Example 2 was repeated except that Polymer A was replaced with 2.7 g. of the triacrylate of the reaction product of trimethylol propane with 20 moles of ethylene oxide. The results were essentially the same in yielding a continuous tone black and white photographic print.

EXAMPLE 15

A photopolymerizable composition was prepared by dissolving 46 g. of monomeric pentaerythritol triacrylate and 5.0 g. 2-ethyl-9,10-anthraquinone in 30 g. of triethylene glycol diacetate. 7 g. of Sterling FT carbon black was added. This photopolymerizable composition was then used in place of the photocurable composition in Example 2. The results were essentially the same as in Example 2.

EXAMPLE 16

15 g. of "DION polymercaptan resin DPM–1002" commercially available from Diamond Alkali Co. having a thiol functionality of 2 to 3 and a molecular weight of about 5,000, 0.36 g. triallyl urea and 1.0 g. carbon black (Sterling FT) in ethylene glycol monoethyl ether were mixed together and then heated in a vacuum oven for 5 minutes at 120° C. 1.0 g. of benzophenone was then added and mixing was continued for 2 minutes. A 1 mil film of this mixture was spread on a sheet of opaque Mylar and a sheet of clear Mylar was rolled on top of the mixture to produce a sandwich. The sandwich (clear side up) was exposed under a continuous tone, photographic negative to a 275 watt U.V. lamp situated 9″ away for 3 minutes. Upon peeling the sandwich apart, a negative image, i.e. one identical to the photographic negative through which the light passed, adhered to the opaque Mylar and a positive continuous tone image, i.e. reversed relative to the negative through which the light passed, formed on the clear Mylar. Uncured polymer was removed from the images by blotting with paper soaked in ethanol. The positive image was then dried and laminated to a piece of high reflectance paper to produce a silverless, black and white, continuous tone, photographic print. The visual appearance of the thus produced print could not be differentiated from a standard silver halide print using the same negative and conventional printing technology.

EXAMPLE 17

Example 2 was repeated except that 18 g. of "DION polymercaptan resin DPM–1002" was substituted for the 0.9 g. of pentaerythritol tetrakis (β-mercaptopropionate). A good silverless, continuous tone, photographic print resulted which could not be differentiated from the standard silver halide print made from the same negative using conventional printing technology.

EXAMPLE 18

Example 9 was repeated except that Polymer A was replaced by 3.8 g. of triallyl urea, 9.8 g. of pentaerythritol tetrakis (β-mercaptopropionate) was used and the image was "developed" by washing with acetone instead of ethanol. The print of the step wedge showed 15 steps and the characteristic curve gave a gamma of 1.1.

EXAMPLE 19

Example 9 was repeated except that Polymer A was replaced by 6.0 g. of an allyl terminated epoxy prepolymer prepared from reacting stoichiometric amounts of diallyl amine and diglycidyl ether of bisphenol A, commercially available from Shell Chemical Co., said prepolymer having a molecular weight of about 616 and 5.0 g. of pentaerythritol tetrakis (β-mercaptopropionate) was used. A characteristic curve generated with a Kodak 21 step wedge consisted of 15 measurable steps with a gamma of 0.92.

EXAMPLE 20

Example 2 was repeated except that Polymer A was replaced by an equal weight of cellulose acetate methacrylate. A good continuous tone photographic print was produced.

EXAMPLE 21

50 g. of "DION Polymercaptan Resin DPM–1002" commercially available from Diamond Alkali Co. having a thiol functionality of 2 to 3 and a molecular weight of about 5,000, 2.5 g. of triallyl cyanurate, and 2.5 g. of carbon black (Sterling FT) in ethylene glycol monoethyl ether were mixed together and then heated in a vacuum oven for 5 minutes at 120° C. 5.0 g. of benzophenone was added to the mixture and mixing was continued for 2 minutes. A 1 mil film of this mixture was spread on a sheet of an opaque Mylar and a sheet of clear Mylar was rolled on top of the mixture to produce a sandwich. The thus formed sandwich, clear side up, was exposed under a continuous tone photographic negative to a 275 watt U.V. lamp situated 9" away for 3 minutes. The sandwich was then peeled apart resulting in a positive image, i.e. one reversed relative to the photographic negative through which the light passed adhering to the clear Mylar. Uncured polymer was removed from the positive image by blotting with paper soaked in ethanol. The positive continuous image was then dried and laminated to a piece of high reflectance white paper to give a silverless, black and white, continuous tone, photographic print. The quality and appearance of the thus formed print was of the same caliber as a standard silver halide print made from the same negative using conventional printing technology. This example illustrated the use of a photosensitive composition containing a monomeric polyene and a polymeric polythiol.

EXAMPLE 22

600 g. (0.22 mole) of a polypropylene ether triol having a molecular weight of 2,960 commercially available under the tradename "Triol 3000" by Union Carbide Corp. was charged to a 1 liter resin kettle along with 0.3 g. of dibutyl tin dilaurate. The kettle was heated to 110° C. under vacuum and maintained thereat for 1 hour. The kettle was cooled to 60° C. whereat 40 g. (0.48 mole) of allyl isocyante was added dropwise from a dropping funnel to the reaction mixture. After 20 minutes the NCO content was 0.80 mg. NCO/g. The thus formed prepolymer was then maintained under vacuum at 70° C. for 1 hour followed by 2 hours at 90° C. This allyl-terminated polymer was identified as Polymer B. 50 g. of Polymer B plus 60 g. of "DION Polymercaptan Resin DPM–1002" and 5 g. of carbon black (Sterling FT) in ethylene glycol monoethyl ether were mixed together and then heated in a vacuum oven for 5 minutes at 120° C. 5.0 g. of benzophenone was then added to the mixture and mixing was continued for 2 minutes. A 1 mil film of this mixture was spread on a sheet of opaque Mylar and a sheet of clear Mylar (1 mil thick) was rolled on top of the photosensitive mixture to produce a sandwich. The thus formed sandwich, clear side up, was exposed through a continuous tone photographic negative in contact therewith to a

275 watt U.V. lamp situated 9" away for 3 minutes. The negative was removed and the sandwich was peeled apart resulting in a positive image, i.e. one reversed relative to the photographic negative through which the light passed adhering to the clear Mylar while a negative image was left on the opaque Mylar. Uncured polymer was removed from the images by blotting with paper soaked in ethanol. The positive, continuous tone image was then dried and laminated to a piece of high reflectance white paper to give a silverless, black and white, continuous tone, photographic print. The quality and appearance of said print could not be differentiated from the standard silver halide print from the same negative using conventional printing technology.

EXAMPLE 23

24.4 g. of pentaerythritol tetrakis (β-mercaptopropionate), 25.6 g. of the reaction product of 1 mole of 1,4-butanediol with 2 moles of allyl isocyanate along with 1.5 g. of carbon black (Sterling FT) in ethylene glycol monoethyl ether were mixed together and then heated in a vacuum oven for 5 minutes at 120° C. 2.5 g. of benzophenone were added to the mixture and mixing was continued for 1 minute. A 1 mil film of this photosensitive mixture was spread onto a U.V. transparent Mylar film (5 mil thick) and a 1 mil thick U.V. transparent Mylar film was rolled on top of the mixture to produce a sandwich. The sandwich with the thin Mylar film up was exposed through a continuous tone photographic negative in contact with the thin Mylar film to a 275 watt U.V. lamp positioned 9" away for 3 minutes. The sandwich was peeled apart and a negative image, i.e. one identical to the photographic negative through which the light passed, adhered to the thick Mylar bottom film and a positive continuous tone image, i.e. reversed relative to the negative through which the light passed, was formed on the thin clear Mylar. The positive image was immersed in an ultrasonic bath containing ethanol at 60° C. for 10 seconds to remove uncured polymer. Both images were then reexposed directly to the 275 watt U.V. lamp for 30 seconds. The thus reexposed positive image was laminated to white pigmented polyvinyl chloride with "Quik Stick" a commercially available spray adhesive to give a silverless, black and white, continuous tone, photographic print of excellent quality.

EXAMPLE 24

27 g. of the triacrylate of the reaction product of one mole of trimethylol propane with 20 moles of ethylene oxide was admixed with 9 g. of pentaerythritol tetrakis (β-mercaptopropionate). 1.5 g. of benzophenone was added to the mixture to form a photosensitive composition and mixing was continued for 2 minutes. The procedure of Example 23 was repeated except that the photosensitive composition prepared in this example was substituted for the photocurable composition used in Example 23. The visual appearance and quality of the photocured polymer print obtained in this example was such that it could not be differentiated from a standard silver halide print made from the same negative using conventional printing technology. This example illustrates the use of a reactive ene group conjugated with another double bond grouping (C=O).

EXAMPLE 25

50 g. of a liquid hydroxy terminated polybutadiene derivative having a molecular weight of about 2200 and a double bond distribution consisting of about 60% trans-1,4; and about 50% cis-1,4; and about 20% vinyl-1,2 (commercially available from Sinclair Petrochemical Inc. under the trade name "Poly B–D–R 45M"), 5 g. of pentaerythritol tetrakis (β-mercaptopropionate) 7.5 g. of carbon black (Sterling FT) were mixed together in ethylene glycol monoethyl ester and heated in a vacuum oven for 5 minutes at 120° C. 5.0 g. of benzophenone were added to the mixture and mixing was continued

for 2 minutes. The procedure of Example 23 was followed except that the photocurable composition herein was substituted for the photocurable composition employed in Example 23. The resultant photocurable polymer print had the visual appearance and quality of a standard silver halide print made from the same negative using conventional printing technology.

EXAMPLE 26

10 g. of a solid SBR Rubber commercially available from General Tire & Rubber Co. under the trade name "Gentro 1002" was dissolved in 50 g. of Decalin (as a solvent). 1 g. of pentaerythritol tetrakis (β-mercaptopropionate), 0.1 g. of silica ("Hi Sil 233") and 0.5 g. of carbon black along with 0.5 g. of benzophenone were then added to the solution and mixing was continued for 3 minutes. The procedure of Example 23 was repeated except that the photocurable composition made up herein was substituted for the photocurable composition used in Example 23. The photocured polymer print obtained in the instant example was such that it could not be differentiated from a standard halide print made from the same negative using conventional printing technology.

EXAMPLE 27

39.8 g. of trimethylolpropane tris (β-mercaptopropionate), 20.1 g. of triallyl cyanurate, 3.0 g. of carbon black and 5.0 g. of benzophenone were admixed in the absence of U.V. light for 2 minutes. The procedure for forming a print of Example 23 was repeated except that the photocurable composition formed herein was substituted for the photocurable composition used in Example 23. The silverless, black and white, continuous tone, photographic print had the same appearance and quality as that made from a standard silver halide print using the same negative employing conventional silver technology. This example illustrates the use of a photocurable composition containing a monomeric polyene and a monomeric polythiol.

EXAMPLE 28

Example 23 was repeated except that the photocurable composition contained 50 g. of Polymer B from Example 22, 60 g. of the polymeric polythiol used in Example 22, 9 g. of carbon black and 10.0 g. of benzophenone. The visual appearance and quality of the photocured polymer photographic print obtained in this example was such that it could not be differentiated from a standard silver halide print using conventional printing technology. This example illustrates the use of a photocurable composition containing a polymeric polyene and a polymeric polythiol.

Conventional photography is restricted either to black and white images which can, at most, be modified to give blue or brown tones or to full color images in which the colors of the final print closely resemble those of the subject matter. In the process described herein, there is no such restriction since, by the use of suitable dyes in the photopolymer and colors in the support to which the image is laminated, any combination of colored images may be obtained in printing any given photographic negative.

The following example shows the versatility of the instant invention in obtaining prints of various colors other than the ordinary black and white print.

EXAMPLE 29

10 g. of Polymer A, 0.9 g. of pentaerythritol tetrakis (β-mercaptopropionate) and 1.5 g. phthalocyanine blue commercially available from Harshaw Chemical Co. in ethylene glycol monoethyl ether were mixed together and then heated in a vacuum oven for 5 minutes at 120° C. 0.2 g. of benzophenone was added to the mixture and mixing was continued for 2 minutes. A 1 mil film of the photocurable mixture was spread on a sheet of opaque Mylar and a sheet of clear Mylar was rolled on top of the photocurable mixture to produce a sandwich. The thus formed sandwich, clear side up, was exposed through a continuous tone photographic negative in contact therewith to a 275 watt U.V. lamp situated 9" away for 3 minutes. The negative was removed and the sandwich was peeled apart, resulting in a positive image, i.e. one reverse to the photographic negative through which the light passed adhering to the clear Mylar while the residual material was left on the opaque Mylar. Uncured polymer was removed from the images by blotting with paper soaked in ethanol. The positive, continuous tone image, i.e. reversed relative to the negative through which the light passed thus formed on the clear Mylar was then dried and laminated to a piece of high reflectance yellow paper to give a silverless, green and yellow, continuous tone photographic print of excellent quality and appearance.

EXAMPLE 30

30 g. of "Ricon 150," a polybutadiene of molecular weight approximately 2000 containing 70% pendant vinyl groupings and sold by the Richardson Co., Melrose Park, Ill., was mixed with 65 g. of pentaerythritol tetrakis (β-mercaptopropionate), 8 g. of benzophenone and 3.2 g. of Sterling FT carbon black. A 1 mil layer of the resulting mixture was laminated between two sheets of clear polyvinyl chloride film and exposed under a continuous tone negative for 1 minute to a 4000 watt pulsed xenon arc lamp 2 feet away. The laminate was stripped apart and the polyvinyl chloride adjacent to the negative was rinsed with ethanol, dried, and laminated to a piece of high reflectance white paper. An excellent continuous tone positive print was produced.

The following example shows a method for producing a photographic continuous tone positive microfilm from a continuous tone negative which does not use silver salts as the imaging medium.

EXAMPLE 31

26.4 g. of Polymer A, 1.82 g. of pentaerythritol tetrakis (β-mercaptopropionate), 1.0 g. of carbon black (Sterling FT) and 2.0 g. of benzophenone were admixed in the absence of U.V. light for 10 minutes. A 1 mil layer of this mixture was laminated between opaque Mylar and 0.005" thick clear Mylar (silverless photographic paper). The thus formed sandwich was exposed through its clear film side and through a microfilm as a negative to a 275 watt U.V. lamp positioned 9" away for ½ minute. The sandwich was peeled apart and the uncured polymer was removed from the positive image on the clear Mylar by immersing same in an ultrasonic bath containing ethanol at 60° C. for 10 seconds. Since attrition of the silverless emulsion would occur with use of the film, a layer of clear Polymer A was cast on top of the cured polymer image and a second layer of 0.005" clear Mylar was laminated to the thus formed microfilm.

EXAMPLE 32

The procedure of Example 3 was employed except that 10 g. of the reaction product of polytetramethyleneether glycol having a molecular weight of about 2,000 and allyl isocyanate in a mole ratio of 1:2 respectively were substituted for the 10 g. of Polymer A. An excellent quality silverless, black and white, continuous tone photographic print resulted.

EXAMPLE 33

The procedure and reactants of Example 3 where employed except that 10 g. of the reaction product of polyoxypropylene glycol sold under the trade name "NIAX" by Union Carbide Co. having a molecular weight of about 2,000, tolylene 2,4-diisocyanate and allyl alcohol in a mole ratio of 1:2:2 respectively was substituted for the 10 g. of Polymer A. The resultant continuous tone, black and white, silverless, photographic print was of excellent quality.

EXAMPLE 34

The procedure and reactants of Example 3 were employed except that 10 g. of the reaction product of a linear solid polyester diol having a molecular weight of about 3200 commercially available from Hooker Chemical Co. under the trade name "Rucoflex S–1011–35" and allyl isocyanate in a mole ratio of 1:2 respectively was substituted for the 10 g. of Polymer A. The resultant silverless continuous tone photographic print was of excellent quality.

EXAMPLE 35

The procedure and reactants of Example 3 were employed except that 10 g. of the reaction product of a phthalate esterol having a molecular weight of about 4200, hydroxyl number of 26.8, 1.22 diester units per mole and being commercially available from Quaker Oats Co. under the trade name "Polymeg 2000 Phthalate Esterol" and allyl isocyanate in a mole ratio of 1:2 respectively was substituted for the 10 g. of Polymer A. The resultant silverless, black and white, continuous tone, photographic print had excellent quality.

EXAMPLE 36

The procedure and reactants of Example 23 were followed except that 31.6 g. of the reaction product of a polytetramethyleneether glycol commercially available from Quaker Oats Co. having a hydroxyl number of 37.1 and a molecular weight of about 3,000 and allyl isocyanate in a mole ratio of 1:2 respectively was substituted for the 25.6 g. of the reaction product of 1 mole of 1,4-butanediol with 2 moles of allyl isocyanate and 2.6 g. trimethylolpropane tris (β-mercaptopropionate) was substituted for the 24.4 g. of pentaerythritol tetrakis (β-mercaptopropionate). The resultant silverless continuous tone photographic print was of excellent quality.

EXAMPLE 37

Example 23 was repeated except that 62.5 g. of the reaction product of a polypropylene glycol having a molecular weight of about 6000 sold under the trade name "Triol 6000" by Union Carbide Corp. and allyl isocyanate in a mole ratio of 1:3 respectively was substituted for the 25.6 g. of the reaction product of 1 mole of 1,4-butanediol and 2 moles of allyl isocyanate and 3.6 g. of ethylene glycol bis (β-mercaptopropionate) was substituted for the 24.4 g. of pentaerythritol tetrakis (β-mercaptopropionate). The resultant silverless, continuous tone, black and white, photographic print had excellent quality.

EXAMPLE 38

Using conventional silver halide film, 3 separation negatives were prepared by photographing an outdoor scene with a 4 x 5 Calcumet View Camera, 6½" Ilex-Calumet Caltar *f*/6.3 lens with the camera mounted on a tripod. The negatives were prepared through the following filters: Wratten #25 (red), Wratten #58 (green) and Wratten #47B (blue). The resulting black and white negatives were developed using conventional silver photography methods.

The negative prepared through the red filter was printed using the reactants of Example 2 except that 1.5 g. of Adpro blue dye was substituted for the 1.5 g. of carbon black. The negative prepared through the green filter was printed using the reactants of Example 2 except that 1.5 g. of Adpro yellow dye was substituted for the carbon black. The negative prepared through the blue filter was printed using the reactants of Example 2 except that 1.5 g. of Adpro red dye was substituted for the carbon black.

For the printing, each negative was placed over its aforestated photosensitive composition of Example 2 sandwiched between a sheet of opaque Mylar and a 1 mil thick sheet of clear Mylar on top in contact with the negative. The sandwich, clear side up, was exposed through the negative to a 275 watt U.V. lamp 9" away for 2¼ minutes for the photosensitive composition containing the blue dye, 3½ minutes for the photosensitive composition containing the red dye and 1 minute for the photosensitive composition containing the yellow dye.

Each sandwich containing the photosensitized composition was then peeled apart and uncured polymer was removed by immersing the positive image for each negative in an ultrasonic bath containing ethanol for 10 seconds. The images were then dried, laminated together in register and thereafter laminated to a white, opaque, reflectance paper to produce a three color silverless, photographic print.

The following example illustrates the use of the process of this invention to prepare a silverless photographic film useful in many commercial graphic arts applications.

EXAMPLE 39

An original line image in black and white was photographed using a process camera containing a silverless photographic film comprising the photosensitive composition of Example 18. The art work was illuminated by reflection copy techniques according to established graphic arts photographic procedures using the radiation from two 4000 watt pulsed xenon arc printing lamps. The exposure time was 5 minutes.

Using essentially the procedure of Example 10, a silverless photographic negative was obtained. The overall time for preparation of the negative (i.e. the combined exposure and development time) was less than 7 minutes and no darkroom was required for this work.

The silverless photographic negative then was used successfully to prepare the following articles: (a) a letterpress printing plate (20 mils image relief) and a lithographic printing plate (0.5 mil image relief) according to the process described in co-pending application No. 674,773 filed Oct. 12, 1967, (b) a photoengraving on metallic zinc using conventional photo-resists and the powderless etching technique (35 mils image relief) as used by photoengravers in the preparation of engravings for conversion to flexographic printing plates and (c) a conventional silk screen element which after exposure and washout was useful for printing by the screen-process printing method.

The following example shows the ability of the instant invention to make enlarged, silverless prints.

EXAMPLE 40

50 g. of Polymer A, 1.88 g. of carbon black (Sterling FT) 4.55 g. of pentaerythritol tetrakis (β-mercaptopropionate) were mixed together and heated in a vacuum oven for 5 minutes at 120° C. 5.0 g. of benzophenone was then added and mixing was continued for 2 minutes. A 1 mil film of this photocurable material was spread on a sheet of opaque Mylar and a 1.0 mil thick sheet of clear Mylar was rolled on top of the material to produce a sandwich. The thus formed sandwich was positioned, clear side up, below a modified Beseler enlarger equipped with a 6" diameter Fresnel lens sz. *f*/2 10"; an *f*/4.5 135 mm. Kodak enlarging Ektanon lens and a 275 watt U.V. lamp. A 35 mm. continuous tone negative was placed in the enlarger and the photocurable material was exposed through the negative to the U.V. lamp in a 3× enlargement for a time sufficient to photocure the polymer. The sandwich was then peeled apart and the positive, continuous tone image, adhering to the clear Mylar, was immersed in an ultrasonic bath containing ethanol at 60° C. for 10 seconds to remove uncured polymer. The cured positive image was dried and laminated to a white pigmented polyvinylchloride sheet with a commercial spray adhesive "Quik Stick" to give a silverless, enlarged, black and white, continuous tone photographic print.

The following example shows the use of the instant invention to make a photographic print and a negative simultaneously.

EXAMPLE 41

50 g. of Polymer A, 1.88 g. of carbon black (Sterling FT), 4.55 g. of pentaerythritol tetrakis (β-mercaptopropionate) were mixed together and heated in a vacuum oven for 5 minutes at 120° C. 5 g. of benzophenone was then added and mixing was continued for 2 minutes. 1 mil layer of this photocurable material was spread on a sheet of clear Mylar (0.5 mil thick) and another 0.5 mil thick sheet of clear Mylar was rolled on top of the material to produce a sandwich. The sandwich was exposed through a conventional, continuous tone negative in contact with one of the clear Mylar sheets to a 275 watt U.V. lamp positioned 9″ away for 5 minutes. The sandwich was peeled apart and a negative continuous tone image, i.e. one identical to the negative through which the light passed adhered to the bottom Mylar sheet and a positive continuous tone image, i.e. reversed relative to the negative through which the light passed, was formed on the top Mylar sheet in contact with the negative. The positive, image containing sheet was immersed in an ultrasonic bath containing ethanol at 60° C. for 10 seconds to remove uncured polymer. The negative image containing sheet was then reexposed directly to a 275 watt U.V. lamp for 30 seconds to further harden the image. The positive image was dried and laminated to a sheet of white pigmented polyvinyl chloride with "Quik Stick," a commercially available spray adhesive to give a silverless, black and white, continuous tone photographic print of excellent quality. The thus reexposed negative image was laminated to clear Mylar film with "Quik Stick" to give a silverless, continuous tone, photographic negative comparable to the conventional, silver halide-containing negative employed to make the print in the instant example.

The following example shows the use of the instant invention to make a half-tone negative from a continuous tone photographic print.

EXAMPLE 42

10 g. of Polymer A, 0.9 g. of pentaerythritol tetrakis (β-mercaptopropionate) and 1.5 g. of carbon black (Sterling FT) were mixed together and then heated in a vacuum oven for 5 minutes at 120° C. 0.15 g. of dibenzosuberone was then added to the mixture and mixed therein for 2 minutes. A 1.0 mil thick layer of this photosensitive material was spread on a film of opaque Mylar and a 1.0 mil thick film of clear, U.V. transparent Mylar was rolled on top of the photosensitive layer to produce a sandwich. The sandwich was put in a film holder behind a Kodak contact screen containing 65 lines per inch. The film holder was placed in a number 4 Xerox camera containing an *f*/16 lens. The camera was focused on a continuous tone black and white print which was illuminated with four 1,000 watt U.V. lamps. The film behind the screen was exposed to the U.V. light reflected from the continuous tone print for a period of 20 minutes. The film sandwich was removed from the film holder, stripped apart and a latent negative half-tone image, i.e. reversed relative to the continuous tone positive print reflecting the U.V. light was formed on the clear Mylar along with uncured polymer. To develop the image, uncured polymer was removed from the thus formed negative by immersing said negative in an ultrasonic bath containing ethanol at 60° C. for 10 seconds.

The thus formed silverless photographic negative was then used successfully to prepare the following articles:

(a) A letterpress printing plate (20 mils image relief) and a lithographic printing plate (0.5 mil image relief) according to the process described in a copending application No. 674,773 filed Oct. 12, 1967.

(b) A photoengraving on metallic zinc using conventional photoresists and the powderless etching technique (35 mils image relief) as used by photoengravers in the preparation of engravings for conversion to flexographic printing prints, and

(c) A conventional silk screen element which after exposure and washout was useful for printing by the screen-process printing method.

The following example shows the use of the instant invention to form an unpigmented image which can thereatfer by selectively dyed in the insolubilized portion of the photosensitized composition to give a continuous tone gradation.

EXAMPLE 43

10 g. of Polymer A, and 0.9 g. of pentaerythritol tetrakis (β-mercaptopropionate) were admixed together and then heated in a vacuum oven for 5 mintes at 120° C. 0.15 g. of benzophenone was added to the mixture and mixing was continued for 2 minutes. A 1 mil layer of this material was spread on a film of opaque Mylar and 1 mil thick film of clear Mylar was rolled on top of the photosensitive layer to produce a sandwich. The sandwich (clear side up) was exposed through a continuous tone negative to a 275 watt U.V. lamp 9″ away for 3 minutes. Upon peeling the sandwich apart, a latent positive continuous tone image, i.e. reversed relative to the negative through which the light passed was formed on the clear Mylar. Uncured polymer was removed from the positive continuous tone image by immersing same in an aultrasonic bath containing ethanol at 60° C. for 10 seconds. The image was dyed by immersing it in a bath of a solution of Nigrogine SSB dissolved in dibutyl Cellosolve for 15 minutes.

EXAMPLE 44

Example 39 was repeated except a half-tone print was photographed to give a half-tone negative.

What is claimed is:

1. A composition for forming a silverless, continuous tone direct reverse photographic image having a gamma of 0.5 to 1.5 on exposure to actinic radiation through a continuous tone transparency consisting essentially of a uniform mixture of (1) a liquid photosensitive material having a viscosity in the range 0–20 million centipoises at 70° C. consisting essentially of a polyene containing at least two reactive unsaturated carbon to carbon bonds per molecule and a polythiol containing at least two thiol groups per molecule, the total combined functionality of the reactive unsaturated carbon to carbon bonds per molecule in the polyene and the thiol groups per molecule in the polythiol being greater thtan 4, (2) 0.0005 to 33% by weight of said composition of a photosensitizer and (3) 1–25% by weight of said composition of a pigment or 0.1–25% by weight of said composition of a dye.

2. The composition according to claim 1 wherein the composition is supported on a U.V. transparent film.

3. The composition according to claim 1 laminated between two films at least one of which is U.V. transparent.

4. The photosensitive material according to claim 1 wherein the polyene is the reaction product of polytetramethylene ether glycol having a molecular weight of about 1,000 polytetramethylene ether glycol having a molecular weight of about 2,000, tolylene diisocyanate and allyl isocyanate in a mole ratio of 1:1:1:2 respectively.

5. The photosensitive material according to claim 1 wherein the polyene is a styrene/butadiene rubber.

6. The photosensitive material according to claim 1 wherein the polyene is the reaction product of polytetramethylene ether glycol having a molecular weight in the range of about 650 to about 6,000 and allyl isocyanate in a mole ratio of 1:2 respectively.

7. The photosensitive material according to claim 1 wherein the polyene is the reaction product of a polyester diol and allyl isocyanate in a mole ratio of 1:2 respectively.

8. The photosensitive material according to claim 1 wherein the polyene is the reaction product of polyoxypropylene diol having a molecular weight in the range of about 700–4000, tolylene 2,4-diisocyanate and allyl alcohol in a mole ratio of 1:2:2 respectively.

9. The photosensitive material according to claim **1** wherein the polyene is the reaction product of a phthalate or succinate esterol derived from polytetramethylene ether glycol and allyl isocyanate having a molecular weight of about 4,000.

10. The photosensitive material according to claim **1** wherein the polyene is the reaction product of polyethylene ether glycol having a molecular weight in the range of about 600 to 6,000 and allyl isocyanate in a mole ratio of 1:2 respectively.

11. The photosensitive material according to claim **1** wherein the polyene is the reaction product of polyoxypropylene triol having a molecular weight in the range of about 3,000 to 6,000 and allyl isocyanate in a mole ratio of 1:3 respectively.

12. The photosensitive material according to claim **1** wherein the polyene is poly-1,3-butadiene.

13. The photosensitive material according to claim **1** wherein the polyene is the triacrylate of the reaction product of trimethylol propane and ethylene oxide.

14. The photosensitive material according to claim **1** wherein the polyene is triallyl urea.

15. The photosensitive material according to claim **1** wherein the polyene is cellulose acetate methacrylate.

16. The photosensitive material according to claim **1** wherein the polyene is the reaction product of 1,4-butanediol and allyl isocyanate in a mole ratio of 1:2 respectively.

17. The composition according to claim **1** which contains in addition a plasticizer, a filler, an odor mask, a light scattering agent or an antioxidant in an amount equal to 0.005 to 500 parts per 100 parts of the photosensitive composition.

18. The composiion according to claim **1** wherein the photosensitizer is a member of the group consisting of benzophenone, acetophenone, acenapthene-quinone, methyl ethyl ketone, valerophenone, hexanophenone, γ-phenyl-butyrophenone, p-morpholinopropiophenone, dibenzosuberone, 4-morpholinobenzophenone, 4′-morpholinodeoxybenzoin, p-diacetylbenzene, 4-aminobenzophenone, 4′-methoxyacetophenone, benzaldehyde, α-tetralone, 9-acetylphenanthrene, 2 acetylphenanthrene, 1-thioxanthenone, 3-acetylphenanthrene, 3-acetylindole, 9-fluorenone, 1-indanone, 1,3,5-triacetylbenzene, thioxanthen-9-one, xanthene-9-one, 7-H-benz [de]anthracene-7-one, 1-naphthaldehyde, 4,4′-bis(dimethylamino) benzophenone, fluorene-9-one, 1′-acetonaphthone, 2′-acetonaphthone, 2,3-butanedione, tert.-butyl anthraquinone, benzoin, benzoin methyl ether, and mixtures thereof.

19. A silverless photographic image having a gamma in the range 0.5–1.5 consisting essentially of a pigment or dye filled cured polythioether in the image area adhered to a transparent support.

20. A silverless photographic print having a gamma in the range 0.5–1.5 consisting essentially of a pigment or dye filled cured polythioether in the image area on a transparent support laminated to an opaque background material.

21. The print according to claim **20** wherein the opaque background material is plastic, paper, wood, metal, cloth, brick, mortar or glass.

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U.S. Cl. X.R.

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