

[54] **DUAL IMAGE FORMATION ON
SEPARATE SUPPORTS OF
PHOTOCURABLE COMPOSITION**

[72] Inventor: Robert J. Bailey, College Park, Md.
[73] Assignee: W. R. Grace & Co
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[52] U.S. Cl.....96/35.1
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[58] Field of Search 96/35.1, 115, 115 P, 36.3

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Primary Examiner—Norman G. Torchin
Assistant Examiner—Edward C. Kimlin
Attorney—Richard P. Plunkett and Kenneth E. Prince

[57] **ABSTRACT**

This invention is directed to forming two silverless continuous tone photographic images from a sandwich comprising two UV transparent outer support layers and a pigment or dye filled photosensitive composition as the inner layer by exposing said composition to actinic radiation e.g., UV light through image-bearing transparencies adjacent each outer support layer to selectively insolublize the UV exposed areas of said composition, peeling said outer support layer apart and removing soluble portions of the composition in the unexposed areas thereby forming a silverless, continuous tone, photographic image on each outer support layer.

14 Claims, No Drawings

DUAL IMAGE FORMATION ON SEPARATE SUPPORTS OF PHOTOCURABLE COMPOSITION

This invention relates to silverless photography.

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. This 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 UV 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 system 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, Dupont 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 continuous tone photographic images and prints which do not contain silver. Another object is to prepare silverless photographic images and prints which can be processed in normal room lighting. Yet another object of the instant invention is to prepare silverless photographic images and prints which do not require costly chemicals in their development. A still further object of this invention is to prepare two separate photographic images from a single photosensitive composition. Other objects will become apparent from a reading hereinafter.

Similarly the invention comprises sandwiching a pigment or dye filled photosensitive composition between two UV transparent support layers, exposing said composition to actinic radiation through an image-bearing transparency adjacent each support layer thereby curing the photosensitive composition in the exposed areas, peeling said support layers apart and removing uncured portions of the composition in the unexposed areas thereof thus forming a silverless, continuous tone, photographic image on each support layer. Said image, if positive, can be laminated to a background material e.g., a high reflectance material such as white-pigmented polyvinyl chloride to give a continuous tone photographic print. Depending upon whether the dye or pigment in the photosensitive composition is black or white, the resulting image will form a photographic print on being laminated to the opposite colored background material.

It is critical in carrying out this invention that the thickness of the photosensitive composition layer be not less than 2 mils. Photosensitive composition layers of less than 2 mils results in the polymer being cured clear through to the other support layer under normal exposure times and conditions which precludes obtaining two images. Thus for the purposes of this invention the photosensitive composition layer should have a uniform thickness ranging from 2 to 50 mils, preferably 2 to 10 mils.

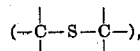
As used herein the term "photosensitive composition" means a composition having a viscosity in the range 0 to 20 million centipoises at 130° C which is solidified either by photocuring or photopolymerization or both on exposure to actinic light.

Photosensitive compositions which are operable in the instant invention are set out in copending applications having U.S. Ser. No. 674,773 filed Oct. 12, 1967, U.S. Ser. No. 779,596 filed Nov. 27, 1968, and U.S. Ser. No. 828,724 entitled "Silverless Photographic Printing Paper" filed May 28, 1969, all assigned to the same assignee and all incorporated by reference herein. In said systems a 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, is cured on exposure to UV light.

As used therein polyenes and polyynes refer to a simple or complex species of alkenes or alkynes having a multiplicity, i.e., at least two "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 double and 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



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

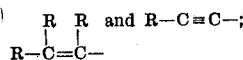


groups when found in aromatic nuclei (cyclic structures exemplified by benzene, pyridine, anthracene, tropolone and the like) which do not under the same conditions react with thiols to give thioether linkages. In the instant invention, products from the reaction of polyenes with polythiols which contain two 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 image is that taught in a copending application having Ser. No. 617,801 filed Feb. 23, 1967, 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



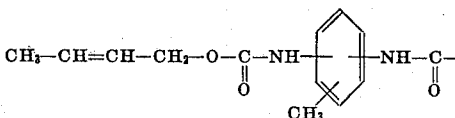
wherein X is a member of the group consisting of



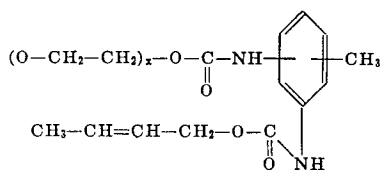
m is at least 2; R is independently selected from the group consisting of hydrogen, halogen, aryl, substituted aryl, cycloalkyl, substituted cycloalkyl, aralkyl, substituted aralkyl and alkyl and substituted alkyl groups containing one to 16 carbon atoms and A is a polyvalent organic moiety free of (1) 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 hetero 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

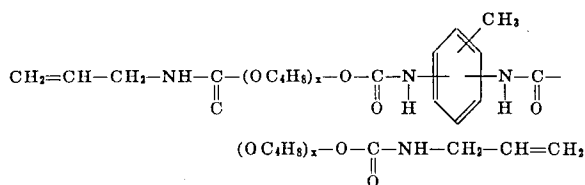
1. crotyl-terminated polyurethanes which contain two "reactive" double bonds per average molecule in a near terminal position of the average general formula:



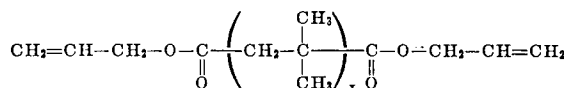
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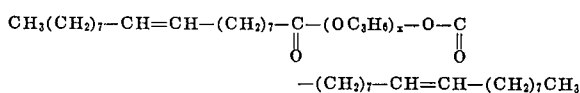
wherein x is at least 1,
2. the following structure which contains terminal "reactive" double bonds:



where x is at least 1,
3. the following structure which contains terminal "reactive" double bonds:



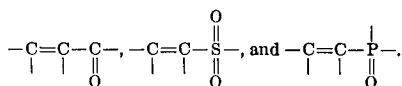
where x is at least 1, and
4. the following structure which contains near terminal "reactive" double bonds:



where x is at least 1.

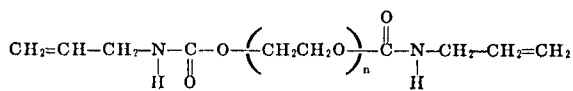
A second group of polyenes operable in the instant invention includes unsaturated polymers in which the double or triple bonds occur primarily within the main chain of the molecules. Examples include conventional elastomers (derived primarily from standard diene monomers) such as polyisoprene, polybutadiene,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



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 1,175, the triacrylate of the reaction product of trimethylolpropane with 20 moles of ethylene oxide and the like.

Another polyene operable in the present invention to form photographic images is



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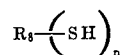
where n is 2 to 135. This polyene, because it is water soluble, is easily developed in a water bath after imaging.

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 viscosity range set out above at 130° C.

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

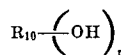
On the average the polythiols must contain two or more —SH groups/molecule. They usually have a viscosity range of 0 to 20 million centipoises (cps) at 130° C. as measured by a Brookfield Viscometer. Included in the term "polythiols" as used herein are those materials which in the presence of an inert solvent, aqueous dispersion or plasticizer fall within the viscosity range set out above at 130° 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

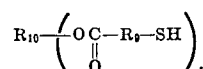


where n is at least 2 and R_3 is a polyvalent organic moiety free from "reactive" carbon to carbon unsaturation. Thus R_3 may contain cyclic groupings and minor amounts of hereto atoms such as N, S, P or O but primarily contains carbon-hydrogen, carbon-oxygen, or silicon-oxygen containing chain linkages free of any "reactive" carbon to carbon 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 formula:



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:



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 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(thioglycolate), 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 polypropyleneether glycol bis(β -mercaptopropionate) which is prepared from polypropyleneether 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 percent of the theoretical value for complete reaction, the functionality (assuming 100 percent pure starting materials) would be 2.0. If, however, the reaction were carried to only 95 percent of theory for complete reaction, about 10 percent 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 percent 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, cross-linked 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 cross-link 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 cross-linked 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 cross-linked 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 cross-linked 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 cross-linked 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 four.

The above systems are preferred. However, any system having an initial viscosity in the range 0-20 million centipoises at 130° 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. Pat. Nos. 2,760,863; 3,380,831, etc., for examples of some of these 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, anti-static agents, flame-retardant 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 dyeing 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. White TiO₂ pigments 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 UV radiation or by other means and can transmit a substantial amount of UV light. Operable plastic include but are not limited to, polyethylene, polypropylene, poly-4-methylpentene, polystyrene "Mylar" i.e., polyethylene terephthalate, cellu-

lose acetate and the like. 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. Support films 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 2,200–4000 Å under ambient conditions or otherwise to 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. Examples of photosensitizers include, but are not limited to, benzophenone, acetophenone, acenaphthene-quinone, methyl ethyl ketone, valerophenone, hexanophenone, α -phenylbutyrophenone, P-morpholinopropiophenone, dibenzosuberone, 4-morpholinobenzophenone, 4'-morpholinodeoxybenzoin, p-diacetylbenzene, 4-aminobenzophenone, 4'-methoxyacetophenone, benzaldehyde, α -tetralone, 9-acetylphenanthrene, 2-acetylphenanthrene, 10-thioxanthene, 3-acetylphenanthrene, 3-acetylindole, 9-fluorenone, 1-indanone, 1,3,5-triacetylbenzene, thioxanthene-9-one, xanthene-9-one, 7-H-benz[de]anthracene-7-one, 1-naphthaldehyde, 4,4'-bis(dimethylamino)benzophenone, fluorene-9-one, 1'-acetophenone, 2'-acetophenone 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 0.005 to 50 percent by weight, suitably 0.0005 to 33 percent by weight, preferably 0.5 to 25 percent, 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 silverbased 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 UV 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 through image-bearing transparencies under ambient or elevated temperature conditions will initiate photocuring in the exposed areas.

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, UV 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.) through image-bearing

transparencies will cure controllably and in a very short time period in the exposed areas 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 temperatures up to 130° 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 on both surfaces of the polymer layer. Likewise, if the material is used in a camera, a continuous tone scene will be rendered as a continuous tone negative on each surface of the polymer layer after independent exposure of each surface. 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 UV through a negative that is in contact with a support layer or the negative image can be projected onto a support layer or the material can be placed in a camera with a support layer towards the lens and exposed like a conventional photographic film and thereafter be reexposed through the other support layer. The photosensitive polymer layer is sandwiched between two transparent support layers of the same or various compositions e.g., glass, quartz, plastic, etc., in which case the laminate can easily be handled in conventional photographic equipment such as cameras, enlargers, contact printing frames, etc.

The development of the exposed film is carried out by peeling the support layers apart and immersing each in an aqueous solution containing a soap or detergent or a solvent, preferably alcohol. Depending on the development bath, i.e., whether water per se or soap or detergent or solvent, etching periods ranging from 5 seconds up to 1 hour or more optionally followed by blotting with a sponge or other mechanical means are employed, followed by drying with 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. Thus it has 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, reduces etching time 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 difference in solubility between the cured areas in the photosensitive layer and the portions of said layer which remain uncured determines the efficiency of the image making process. Also, the quicker the exposed area becomes insoluble the more efficient the process. That is, the faster the

cross-links in the photocurable composition are formed, the quicker a gel structure is developed with its resulting insolubility in selective etching or wash-out solvents.

The solvent used for washing (i.e., developing the image) of the photosensitized plate made from the photocurable compositions is primarily a diluent which reduces the viscosity of the uncured mixture so that it is easily removed. Removal can be speeded up, where necessary, by blotting with a sponge and the like. The washing liquid is selected so that it is readily miscible with or emulsified with the uncured material, yet has little action on the cured image or polymer support. The preferred solvent liquids are water or water and a detergent and/or soap. Alcohols, such as ethanol, methanol or mixtures of methanol and/or ethanol, with methyl, ethyl or propyl acetate are also operable for a large number of photocurable compositions. Other solvents with high evaporation rates are well known to those skilled in the art. It should be noted herein that the term "solvent" includes not only organic solvents but also water and other aqueous systems wherein the unexposed photocurable layer is soluble (including dispersible in said systems and the photocured portion is not so affected. The use of aqueous systems as a solvent in the instant invention is advantageous not only economically but also because of the elimination of the hazards involved in handling organic solvents. In those instances where the photocurable layer is acidic or basic the image can be developed by dissolving or dispersing the unexposed areas in an aqueous system of the opposite polarity, i.e., to use an aqueous acidic solvent system with a basic photocurable layer and vice versa. A specific example of such a system would be the use of an aqueous acidic developer such as a 20 percent aqueous acetic acid solution with a photocurable layer comprising a polyene containing basic amino groups in its structure. Conversely, an aqueous alkaline developer, e.g., dilute aqueous sodium hydroxide would be used with a photocurable layer containing acidic thiol groups. Obviously the degree of acidity or alkalinity should not be allowed to reach those levels wherein the essentially completely photocured areas are attacked. It is also possible in the instant invention to wash at elevated temperatures wherein the solid uncured portion of the photocurable composition melts and is removed as a liquid.

A convenient method of carrying out the process of this invention is to place separate image bearing positive or negative continuous tone transparencies in contact frames parallel to both surfaces of a layer of a pigment or dye filled photosensitive composition, i.e., photocurable or photopolymerizable composition or both which has been sandwiched between transparent support layers and adjusted for uniformity of height by suitable means, e.g., a drawbar, precast mold and the like. The layer of the photosensitive composition is exposed through each transparency and the transparent support layers to sources of actinic light suitably in the wavelength range of 2,200–4,000 Å, until the layer on both of its surfaces is cured or polymerized or both to an insoluble stage in the exposed areas.

To develop the images, the two support layers are pulled apart and each is immersed in an appropriate water or solvent bath to remove the uncured or unpolymerized photosensitive composition from the unexposed areas. In some instances, development is speeded up by emergizing the development medium with ultrasonic energy. The photographic transparencies are 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 UV radiation for periods up to 10 minutes to further harden it.

The resulting images on their transparent supports 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.

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 UV radiation for adhe-

sion. Ordinarily transparent adhesives are also operable and do not require UV 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, vinyl and any other black or 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.

When practicing the instant invention, the amount of dye or pigment can be added over fairly wide ranges. For example, 1 to 25 percent by weight of the photosensitive composition of a pigment can be added to obtain good quality, continuous tone, photographic images. In the case of the dye, 0.1 to 25 percent by weight of the photosensitive composition of a dye is employed to obtain continuous tone photographic images.

It is also possible to carry out the invention by exposing the sandwich containing the photosensitive composition to one source of UV light through one of its support layers and a continuous tone image-bearing transparency to obtain a latent image on one of the supports and thereafter turn the sandwich over and expose the other surface of the photosensitive composition through the same or different continuous tone image-bearing transparency and obtain a latent image on the other support. The supports are then pulled apart as previously stated and developed by immersing each in a bath which will remove the soluble unexposed photosensitive composition.

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

FORMATION OF POLYENE PREPOLYMER

EXAMPLE 1

458 g. (0.23 moles) of a commercially available liquid polymeric diisocyanate sold under the trade name "Adiprene L-100" by E. I duPont de Nemours & Co. was charged to a dry resin kettle maintained under a nitrogen atmosphere and equipped with a condenser, stirrer, thermometer, and gas inlet and outlet. 37.8 g. (0.65 moles) of allyl alcohol was charged to the kettle and the reaction was continued for 17 hours with stirring at 100° C. Thereafter the nitrogen atmosphere was removed and the kettle was evacuated 8 hours at 100° C. 50 cc. dry benzene was added to the kettle and the reaction product was azeotroped with benzene to remove the unreacted alcohol. This allyl terminated liquid prepolymer had a molecular weight of approximately 2,100 and will be referred to as Prepolymer A hereinafter.

EXAMPLE 2

400 g. (0.2 moles) of "Adiprene L-100" was charged to a dry resin kettle maintained under nitrogen and equipped with a condenser, stirrer, thermometer and gas inlet and outlet. 25.2 g. (0.43 moles) of propargyl alcohol ($\text{HC}=\text{C}-\text{CH}_2\text{OH}$) was added to the kettle and the reaction was continued with stirring for 18 hours at 160° C. Thereafter the nitrogen atmosphere was removed and the kettle was evacuated 16 hours at 100° C. followed by azeotropic distillations with 50 cc. water and then 50 cc. benzene to remove any excess propargyl alcohol. This H=C-terminated liquid prepolymer had a viscosity of 27,500 centipoises at 70° C. and a molecular weight of 2,100 and will be referred to as Prepolymer B hereinafter.

EXAMPLE 3

1 mole of commercially available polyethylene glycol having a molecular weight of 1,450 and a specific gravity of 1.21 was charged to a resin kettle maintained under nitrogen and equipped with a condenser, stirrer, thermometer and a gas inlet and outlet. 2.9 g. dibutyl tin dilaurate as a catalyst was charged to the kettle along with 2 moles tolylene-2,4-diisocyanate and 2 mols of allyl alcohol. The reaction was continued with stirring at 60° C. for 2 hours. Thereafter a vacuum

of 1 mm. was applied for 2 hours at 60° C. to remove the excess alcohol. This $\text{CH}_2 = \text{CH}-$ terminated prepolymer had a molecular weight of approximately 1950 and will hereinafter be referred to as Prepolymer C.

EXAMPLE 4

1 mole of a commercially available polyoxypropylene glycol having a molecular weight of about 1958 and a hydroxyl number of 57.6 was charged to a resin kettle equipped with a condenser, stirrer, thermometer and a gas inlet and outlet. 4 g. of dibutyl tin dilaurate as a catalyst was added to the kettle along with 348 g. (2.0 moles) of tolylene-2,4-diisocyanate and 116 g. (2 moles) of allyl alcohol. The reaction was carried out for 20 minutes at room temperature under nitrogen. Excess alcohol was stripped from the reaction kettle by vacuum over a 1 hour period. The thus formed $\text{CH}_2 = \text{CH}-$ terminated liquid prepolymer had a molecular weight of approximately 2,400 and will hereinafter be referred to as Prepolymer D.

EXAMPLE 5

750 g. of a N-containing tetrol (hydroxyl functionality = 4) available from Wyandotte Chemicals Corp. under the trade name "Tetronic Polyl 904" having a M.W. of 7,500 was placed in a reaction vessel heated at 110° C. The flask was maintained under vacuum for 1 hour. Then, under an atmosphere of nitrogen, 0.1 cc. dibutyl tin dilaurate was added and the flask was cooled to 50° C. Now 18.3 g. allyl isocyanate was added slowly, maintaining the temperature at about 95° C. for about 1 hour after the addition was completed. The thus formed polymeric polyene (i.e., Prepolymer E hereinafter) had a theoretical allyl functionality of 2.2, a theoretical hydroxyl functionality of 1.8, and a calculated molecular weight of about 7,683.

EXAMPLE 6

To a resin kettle maintained under a nitrogen atmosphere and equipped with a condenser, stirrer, thermometer and gas inlet and outlet was added 843 g. of a commercially available liquid diisocyanate prepolymer sold under the trade name "Multirathane F-196" by Mobay Chemical Co., said prepolymer having a molecular weight of about 1,680 and an available isocyanate content of 4.7 - 5.2 percent. 87 g. (1.5 moles) of allyl alcohol was added to the kettle and the reaction was continued for 18 hours at 140° C. with stirring. Thereafter the nitrogen atmosphere was removed and the kettle was evacuated for 22 hours at 100° C. 50 cc. of dry benzene was added to the kettle and the reaction product was azeotroped therewith to remove any unreacted alcohol. This $\text{CH}_2 = \text{CH}-$ terminated liquid prepolymer had a viscosity of 25,000 centipoises at 70° C. and a molecular weight of approximately 1,800 and will be referred to as Prepolymer F hereinafter.

EXAMPLE 7

678 g. (0.34 moles) of a commercially available polyoxypropylene glycol sold under the trade name NIAx by Union Carbide Co. and having a molecular weight of about 2,025 was degassed for 2 hours at 100° C. and thereafter charged to a resin kettle maintained under a nitrogen atmosphere and equipped with a condenser, stirrer, thermometer and gas inlet and outlet. 118 g. (0.68 moles) of tolylene 2,4-diisocyanate was charged to the kettle and the reaction was heated with stirring for 2 3/4 hours at 120° C. After cooling, 58 g. (1.0 moles) of allyl alcohol was added to the kettle and the mixture was refluxed at 120° C. for 16 hours under nitrogen. Excess allyl alcohol was removed overnight by vacuum at 100° C. Half of the allyl terminated liquid prepolymer having a viscosity of 19,400 cps. at 30° C. as measured on a Brookfield Viscometer was removed from the kettle. The other half portion of the prepolymer was combined with 50 cc. of dry benzene and azeotroped overnight following which excess benzene was pulled out under vacuum for 5 hours at 120° C. This portion of the allyl-terminated liquid prepolymer had a viscosity of 1,560 cps. at 70° C. as measured on a Brookfield Viscometer and a molecular weight of approximately 2,500 and will hereinafter be referred to as Prepolymer G.

EXAMPLE 8

751 g. (0.38 moles) of a commercially available polyoxypropylene glycol sold under the trade name "Pluracol P 2010" by Wyandotte Chemical Co. was degassed at room temperature for 3 hours and then charged to a dry resin kettle maintained under a nitrogen atmosphere and equipped with a condenser, stirrer, thermometer and gas inlet and outlet. 132 g. (0.76 moles) of tolylene-2,4-diisocyanate was charged to the kettle and the kettle was heated for 2 hours at 120° C. with stirring under nitrogen. After cooling 58 g. (1.0 moles) of allyl alcohol was added and the mixture was refluxed at 120° C. overnight. Excess allyl alcohol was stripped by vacuum overnight at 120° C. The thus formed allyl terminated liquid prepolymer had a viscosity of 1,500 cps. as measured on a Brookfield Viscometer at 70° C. and a molecular weight of approximately 2,500 and will hereinafter be referred to as Prepolymer H.

EXAMPLE 9

To a liter resin kettle equipped with stirrer, thermometer, gas inlet and outlet and heated to a temperature of 50° C. was charged 610 g. (0.2 moles) of polytetramethylene ether glycol, commercially available from Quaker Oats Co. and having a hydroxyl number of 37.1 along with 0.3 g. dibutyl tin dilaurate. The temperature of the kettle was raised to 100° C. and the contents were freed of water under 1 millimeter vacuum for 1 hour. The resin kettle was cooled to 60° C. and the system was placed under a protective atmosphere of nitrogen throughout the remainder of the reaction. 25.2 g. of allyl isocyanate, (0.4 mole) was added dropwise to the kettle at such a rate as to maintain the temperature at 60° C. When the NCO content dropped to 0.54 mg./g., 1 mm. vacuum again was applied and the system was heated at 70° C. for one hour. The thus formed polymer product i.e., Prepolymer I, was a solid at room temperature but at 50° C. is clear and pourable. The polymer product had a viscosity of 1,800 centipoises at 70° C. as measured on a Brookfield Viscometer and an average molecular weight of approximately 3,200.

EXAMPLE 10

To a 1 liter resin kettle equipped with stirrer, thermometer, gas inlet and outlet was charged 591 g. (0.30 moles) of a polyoxypropylene glycol commercially available from Union Carbide under the trade name "PPG 2025" and 0.3 g. of dibutyl tin dilaurate. The kettle was heated to 110° C. and the contents were freed of water under 1 mm. vacuum for 1 hour. The kettle was cooled to 25° C. and the system was placed under a protective atmosphere of nitrogen throughout the remainder of the reaction. 53.1 ml. (49.8 g., 0.6 moles) of allyl isocyanate commercially available from Chemetron Corp. was added to the system. An exotherm carried the temperature to 45° C. in 22 minutes. After 60 minutes, the NCO content (as determined by titration) was 0.04 mg./g. The system was placed under 1 mm. vacuum and heated to 70° C. to remove traces of unreacted allyl isocyanate. The resultant polymer product had a viscosity of 600 centipoises at 30° C. as measured on a Brookfield Viscometer and an average molecular weight of approximately 2,200 and will hereinafter be referred to as Prepolymer J.

The next two examples show a method of preparing the polyenes of the instant invention by dehydration of polyether glycols.

EXAMPLE 11

100 g. of polypropylene glycol commercially available from Union Carbide under the trade name "PPG 2025" was poured through a hot tube filled with aluminum oxide at such a rate that the entire reaction took place in 2 hours. The tube was 1 inch in diameter with the reaction zone 1-ft. long and completely enclosed within a tube furnace. The alumina catalyst was 10-18 mesh and was maintained at 350° C. using a Lindberg Hevi-Duty tube furnace. The tube was fitted with a dropping funnel and a nitrogen inlet at the top. Nitrogen pressure was kept on the system throughout the reaction. The product collected from the bottom of the tube was analyzed for unsaturation by the mercuric acetate titration method and was found to have 100 percent of the theoretical amount of

unsaturation expected after dehydration of both terminal hydroxyl groups of the polypropylene ether glycol. The polyene product had a viscosity of 125 cps. at 70° C. and an average molecular weight of approximately 2,000 and will hereinafter be referred to as Prepolymer K.

EXAMPLE 12

1 kilogram of polypropylene ether glycol commercially available from Union Carbide under the trade name "PPG 2025" was heated to 120° C. in a round bottom flask. To this was added 120 ml. (20 percent excess) of acetic anhydride at such a rate that the temperature of the mixture was kept at 120°-140° C. Following the addition, the mixture was heated at 140° C. for 4 hours. It was then cooled and diluted with an equal volume of chloroform, washed with 10 percent aqueous sodium carbonate, then with water. The organic layer was separated and the chloroform was removed by distillation. Infrared analysis of the purified material showed it to be the diacetate of the polypropylene glycol with no residual hydroxyl groups.

100 g. of this diacetate was put through the hot tube as in Example 11 except that the packing was glass helices instead of alumina and the temperature was 375° C. The product contained 64 percent of the theoretical amount of unsaturation expected after the elimination of acetic acid from both terminal acetoxy groups of the polypropylene glycol diacetate. The polymer will hereinafter be referred to as Prepolymer L.

EXAMPLE 13

114 g. of hexol sold under the trade name "NIAx Polyol LS-490" by Union Carbide Chemicals Co. having a molecular weight of 684 was charged to a 1 liter 4 neck flask and heated to 110° C. under vacuum and nitrogen for 1 hour. It was then cooled to approximately 60° C. where at 0.1 cc. of dibutyl tin dilaurate was added followed by slowly adding 83 g. (1 mole) of allyl isocyanate to keep the temperature in the range 70°-80° C. during the addition. After addition, the reaction was allowed to continue for 1 hour at 70° C. The polymeric hexaene product i.e., Prepolymer M, had an average molecular weight of approximately 1,200 and a viscosity of 300 centipoises at 70° C.

EXAMPLE 14

To a 1 liter 4 neck flask was charged 300 milliliters of dimethylformamide, 35 g. of tolylene-2,4-diisocyanate and 0.1 cc. of dibutyl tin dilaurate. A mixture of 11.6 g. of allyl alcohol and 22.8 g. of hexol commercially available from Union Carbide Chemical Co. under the trade name "NIAx Polyol LS-490" having a molecular weight of 684 was slowly added to the flask. Temperature was kept at approximately 65° C. during the addition and for a period of 1 hour. The polymeric product obtained had an average molecular weight of approximately 2,100 and will be referred to as Prepolymer N hereinafter.

EXAMPLE 15

To a 1 liter 4 neck flask was charged 100 cc. of dimethylformamide, 100 g. of tolylene-2,4-diisocyanate and 0.1 cc. dibutyl tin dilaurate. 58 g. of hexol, i.e., "NIAx Polyol LS-490" by Union Carbide and 34 g. of allyl alcohol were mixed together and added dropwise to the flask. Before the addition to the flask was completed, the reaction, which was exothermic, gelled and the addition was discontinued.

A comparison of Examples 13, 14 and 15 shows that Example 13 is an improvement over Examples 14 and 15 in that it allows one to form polymer without the necessity of a solvent. A comparison of Examples 14 and 15 shows that when starting with a highly functional polyol using the diisocyanate/allyl alcohol technique one must operate in dilute solution to avoid premature cross-linking (i.e., gelation) which renders the polyene product useless as a curable liquid prepolymer. This problem is avoided completely by using the monoisocyanate technique illustrated in Example 13.

EXAMPLE 16

In a 1 liter, 4 neck flask 220 g. of hexol commercially available from Union Carbide Chemicals Co. under the trade name "NIAx Polyol LS-490" (0.32 moles) and 0.1 cc. of dibutyl tin

dilaurate was heated to 110° C. under vacuum for 1 hour. After cooling in nitrogen to approximately 60° C., 80 g. of allyl isocyanate was added to the flask by means of a dropping funnel. The exothermic reaction produced a temperature of 100° C. When the addition was complete the reaction was continued at 70° C. for 1 hour. The resulting triene polymer product had an average molecular weight of approximately 950 and a viscosity of 300 centipoises as measured on a Brookfield Viscometer at 70° C. and will be referred to as Prepolymer O hereinafter.

EXAMPLE 17

To a 1 liter 4 neck flask was charged 300 g. of a polyester diol (molecular weight 3,232) sold under the trade name "RC Polyester S 101-35" by R. C. Division, Hooker Chemical Corp. The flask was heated to 110° C. under vacuum and maintained thereat for 1 hour. The flask was cooled to approximately 60° C., nitrogen was admitted, and 7.7 g. allyl isocyanate and 8.1 g. of tolylene-2,4-diisocyanate was added by means of a dropping funnel to the reaction at a moderate rate. A maximum temperature of 90° C. was needed. When the addition was complete, the reaction was allowed to continue at 70° C. for 1 hour. The thus formed solid polymeric product had an average molecular weight of approximately 6,800 and a viscosity of 13,600 centipoises when measured on a Brookfield Viscometer at 70° C. and will be referred to as Prepolymer P hereinafter.

EXAMPLE 18

To a 1 liter 4 neck flask heated at 110° C. was charged 808 g. of a polyester diol (having a molecular weight 3,232) sold under the trade name "RC Polyester S 101-35" by R.C. Division Hooker Chemical Corp. and 0.1 cc. dibutyl tin dilaurate. The flask was maintained under vacuum at 110° C. for 1 hour. The flask was cooled to approximately 50° C. and with nitrogen passing through, a mixture of 10 g. of allyl alcohol and 60 g. of tolylene-2,4-diisocyanate was added via a dropping funnel at a moderate rate. The reaction was allowed to continue for 15 minutes. A maximum temperature of 90° C. was produced by the exothermic reaction. The polymeric product obtained was a solid at room temperature but liquid at 70° C. The product had an average molecular weight of approximately 10,500 and a viscosity of 270,000 centipoises at 70° C. and will be referred to as Prepolymer Q hereinafter.

EXAMPLE 19

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 2000, 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 Prepolymer R.

EXAMPLE 20

To a 2 liter flask equipped with stirrer, thermometer and gas inlet and outlet was charged 200 grams of a polyethyleneether glycol having a molecular weight of 400 (0.5 moles) and 100 grams of a polyethyleneether glycol having a molecular weight of 4,000 (0.025 moles). Stirring was commenced and the flask was heated to 60° C. The flask was evacuated with a vacuum pump to remove any water present. After evacuation, two drops of dibutyl tin dilaurate (catalyst) was added and 100 ml. of allyl isocyanate was added by means of an addition funnel over a 2-hour period. The reaction was continued at about 60° C. for 8 hours. The flask was then reevacuated by means of vacuum to remove excess allyl isocyanate. The thus formed

allyl-terminated polymer, i.e., N,N'-diallyl urethane of poly(ethylene oxide) will hereinafter be referred to as Prepolymer S.

EXAMPLE 21

1 mole diglycidyl ether of Bisphenol A having a molecular weight in the range 370-384 and being commercially available from Shell Chemical Co. under the trade name "Epon 828" and 2 moles of diallylamine were stirred in a beaker at room temperature (25° C.). The reaction was continued for 18 hours during which time the exotherm and reaction temperature was maintained below 80° C. The resultant liquid polyene prepolymer will hereinafter be referred to as Prepolymer T.

EXAMPLES 22-41

Table 1 shows various photosensitive compositions which are operable to obtain two images simultaneously on exposure to UV light through an image-bearing transparency adjacent each support layer. The prepolymers from examples 1-21 were admixed with various polythiols, photosensitizers and a dye or pigment in the absence of UV light for periods ranging from 2 minutes to 24 hours or more in order to obtain a homogenous mixture. A 2 mil layer of these mixtures was uniformly spread on a UV transparent support layer and another UV transparent support layer was rolled on top of the photosensitive admixtures to produce a sandwich. Each support layer was 5 mils thick unless otherwise noted.

The thus formed sandwich was then exposed simultaneously to 2 sources of actinic radiation, e.g., UV light, through image-bearing transparencies adjacent and in contact with each support layer of the sandwich. Said exposure causes the photosensitive layer to become insolubilized in the exposed areas on each surface of the photosensitive layer within periods ranging from about 1 second to about 10 minutes.

The image was then developed in various solvents by pulling apart the two support layers and immersing each in an appropriate solvent to remove the uncured soluble photosensitive mixture from the unexposed areas. The development bath was maintained at temperatures ranging from 20° to 65° C. Thereafter each support layer with the image thereon was dried in air or in an oven at elevated temperatures up to about 150° C. The dry images were then laminated to white-pigmented polyvinyl chloride sheets with a commercial spray adhesive "QUIK-STICK" or a UV curable adhesive to give a silverless, black and white,

EXAMPLE 42

10 g. of prepolymer S from Example 20, 4.5 g. of pentaerythritol tetrakis (β -mercaptopropionate) and 1.5 g. carbon black (Sterling FT) in ethylene glycol monoethylether were mixed together and then heated in a vacuum oven for 5 minutes at 120° C. 1.0 g. of dibenzosuberone was then added and mixing was continued for 2 minutes. A 3 mil thick layer of this photosensitive admixture was spread on a sheet of cellulose acetate 5 mil thick and another 5 mil thick sheet of cellulose acetate was rolled on top of the photosensitive admixture to produce a sandwich. The sandwich of the photosensitive material was cut to 5x4 inches and the edges sealed by brief exposure to UV light. The "film" so obtained was loaded into Graphic cut film holders and inserted in a Polaroid MP 4 Technical camera fitted with a Goerz Dagor lens. Illumination of the subject (a watch lying on a three-color picture as background) was supplied by two 275 watt sunlamps. Exposure as 10 to 15 minutes at f 4.5. The film was then removed from the camera and turned over so that the other surface faced the lens. Under the same conditions of illumination a different subject (an ashtray lying on a three-color picture as background) was photographed for 15 minutes at f 4.5. The film was removed from the camera, peeled apart and each support layer was water-washed (60° C.) for a period of 5 minutes. The silverless photographic images obtained on each support were laminated to a white-pigmented polyvinyl chloride sheet with a commercial spray adhesive to give clear, silverless, black and white, continuous tone, photographic prints of excellent quality.

It is obvious that the photographic film of the instant invention which yields two images from a single layer of the photosensitive composition could readily be inserted in present day cameras with little or no adjustment to the camera mechanism. That is, in a conventional camera after a roll of the film is finished on one side it could be turned over and reused on the other side before development and processing. Conventional silver halide film would need an intervening layer between each layer of silver halide to obtain two images from the same frame on the film.

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

EXAMPLE 43

Using the photosensitive composition of Example 42, the sandwich was put in a film holder behind a Kodak contact screen containing 65 lines per inch. The film holder was

TABLE I

Example No.	Pre-polymer, type ¹	Polythiol		Photosensitizer		Dye or pigment		Support layers ³	UV light exposure		Development		Comparative rating of print
		Type ²	Gms.	Type	Gms.	Type	Gms.		Watts ⁴	Time, min.	Bath	Time, min.	
22.....	A	Q-43	11.6	Benzophenone...	10	Carbon black...	15	X	275	2	Ethanol.....	3	Excellent.
23.....	B	Q-43	23.2	do.....	10	do.....	15	X	275	2	do.....	3	Fair.
24.....	C	Q-43	13.8	do.....	10	do.....	15	X	275	3	Water.....	5	Excellent.
25.....	D	Q-43	10.2	Acetophenone...	10	do.....	12	Y	275	4	Isopropanol...	3	Good.
26.....	E	Q-43	3.5	do.....	7.5	do.....	12	Y	4000	.20	do.....	5	Poor.
27.....	F	Q-43	13.5	do.....	10	do.....	10	Y	275	6	do.....	3	Fair.
28.....	G	Q-43	9.8	do.....	10	do.....	7.5	X	275	5	do.....	3	Good.
29.....	H	Q-43	9.8	Benzophenone...	10	Dye ⁵	10	X	4000	.25	Ethanol.....	3	Do.
30.....	I	Q-43	7.6	Dibenzo-suberone.	10	Carbon black...	7.5	X	4000	.20	Isopropanol...	2	Excellent.
31.....	J	P-33	12.1	do.....	12.1	do.....	7.5	Z	4000	.20	do.....	2	Good.
32.....	K	Q-43	12.2	Benzophenone...	10	do.....	10	Z	4000	.33	Ethanol.....	3	Fair.
33.....	L	Q-43	20.0	do.....	10	do.....	10		4000	2	do.....	3	Poor.
34.....	M	P-33	66.3	do.....	10	do.....	10	Z	4000	.20	do.....	5	Fair.
35.....	N	P-33	37.9	Dibenzo-suberone.	10	do.....	10	Z	275	3	do.....	5	Do.
36.....	O	P-33	42.0	do.....	7.5	Titanila ⁶ ...	10	Z	4000	.25	do.....	5	Do.
37.....	P	Q-43	3.6	do.....	7.5	Carbon black...	10	Z	4000	.20	do.....	5	Do.
38.....	Q	Q-43	1.16	do.....	10	do.....	7.5	Z	4000	.40	do.....	10	Do.
39.....	R	Q-43	7.7	do.....	10	do.....	15	Z	4000	.20	Isopropanol...	5	Excellent.
40.....	S	Q-43	40.0	do.....	10	do.....	7.5	Z	4000	.03	Water.....	5	Do.
41.....	T	Q-43	55.0	Benzophenone...	7.5	do.....	7.5	X	4000	.03	Isopropanol...	10	Good.

¹ All prepolymers are those identified by letter in examples 1-21. 100 g. of Prepolymer was used in each of the examples in Table I.

² "Q-43" Pentaerythritol tetrakis (β -mercaptopropionate) and "P-33" Trimethylolpropane tris (β -mercaptopropionate).

³ Support layers are either (X=polyethylene); (Y=polyethylene terephthalate) or (Z=cellulose acetate); all films each 5 mils thick.

⁴ UV light source either a 275 watt type RS sun lamp 9 inches away or a 4000 watt Ascorlux Xenon arc lamp 19 inches away.

⁵ Dye=Aquaprint 05-5207 Black K commercially available from Interchemical Co.

⁶ Continuous tone positive transparencies used when pigment is white TiO₂.

continuous tone, photographic print. (A comparative rating of the resultant print along with the data for the examples is shown in Table I.

placed in a No. 4 zerox camera containing a f 16 lens. The camera was focused on a continuous tone, black and white

print which was illuminated with four 1,000 watt UV lamps. The film behind the screen was exposed to the UV light reflected from the continuous tone print for a period of 5 minutes. Thereafter the film was removed from the camera and turned around so that the other surface of the photosensitive composition could be exposed through its other support film for an additional period of 5 minutes. The film sandwich was removed from the film holder, stripped apart and washed with water at 60° C. for a period of 5 minutes, on each support layer.

The thus formed silverless photographic negatives were then used successfully to prepare the following articles:

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

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 plates, and

c. a conventional silk-screen element which after exposure and wash-out was useful for printing by the screen process printing method.

The following example shows a method of using the instant invention in making enlarged black and white prints.

EXAMPLE 44

A 35 mm. black and white negative was projected using a home-slide projector, i.e., Kodak Carousel 750 manufactured by Eastman Kodak Co. onto a sandwich of the photosensitive composition of Example 42 so that the image was 8×10 inches in size. The projector was equipped with a 500 watt DEK 120 volt 60 cycle lamp which yielded an intensity of 380 microwatts/centimeter² at the enlarged area. After an exposure of 10 minutes, the film was turned over and another 35 mm. black and white negative was projected on the other side of the photosensitive composition for a period of 10 minutes under the same conditions as set out heretofore. The film was then peeled apart and each support layer was washed in warm water (60° C.) for a period of 5 minutes to develop the image. The resulting transparencies were laminated to white pigmented polyvinyl chloride sheets to yield black and white prints. It is to be understood that the negative to be enlarged by this process can be a halftone, continuous tone, or line negative. Additionally, color negatives or transparencies can be enlarged into black and white prints by the practice of this example.

The following examples represent a significant and notable departure from the ordinary concept of black and white photographic imaging materials and processes. This highly unusual situation arises because the photosensitive contrast-forming medium supported on the film base leads, on development, to a white-on-clear supported image rather than the customary black-on-clear supported image. This effect (as noted in the following examples) is accomplished by using a white-pigmented photocurable composition as the image-forming, contrast-forming photosensitive medium.

The next result obtained by working with white-on-clear supported images is that these unusual photographic elements do not behave in a "conventional" manner. For example, a white-on-clear silverless photographic negative on contact printing with ordinary silver halide paper will lead to a negative print rather than a positive. Similarly, if it is printed on the black-pigmented photocurable composition printing paper of this invention, the resulting print will be a negative print.

EXAMPLE 45

30 g. of Prepolymer R from Example 19, 2.72 g. of pentaerythritol tetrakis (β -mercaptopropionate), 3.0 g. titanium dioxide pigment and 3.0 g. of dibenzosuberone were mixed together and then heated in a vacuum oven for 2 minutes at 120° C. A 2 mil film of this material was spread on a sheet of UV transparent cellulose acetate (5 mil thick) and a 5 mil thick of UV transparent cellulose acetate was rolled on top of

the photosensitive material to produce a sandwich. The sandwich was exposed under a continuous tone photographic negative to a 4,000 watt pulsed xenon arc lamp 19 inches away for 5 seconds. The sandwich was then turned over and reexposed to the same lamp for another 5 seconds. Thereafter the sandwich was peeled apart and the uncured portion of the photosensitive composition was washed away in warm water maintained at a temperature 60° C. The thus formed negatives can now be used repetitively to produce positives by the contact method shown in this example by employing a black pigment or dye in the photosensitive composition used herein in place of the TiO₂.

EXAMPLE 46

Example 45 was repeated except that a positive transparency was used instead of the negative. The resultant images on the cellulose acetate supports after washing were laminated to a glossy black background paper to give a direct positive continuous tone, black and white, photographic print.

EXAMPLE 47

Example 46 was repeated except that a positive color transparency was used instead of the positive black and white transparency. The resultant silverless, black and white continuous tone photographic prints were of good quality.

EXAMPLE 48

A 35 mm. positive color transparency was projected using a home-slide projector, i.e., Kodak Carousel 750 manufactured by Eastman Kodak Co. onto a sandwich of the photosensitive composition of Example 45 so that the image was 8×10 inches in size. The projector was equipped with a 500 watt DEK 120 volt 60 cycle lamp which yielded an intensity of 380 microwatts/centimeter² at the enlarged area. After an exposure of 10 minutes on each side of the photosensitive composition, the sandwich was peeled apart and the uncured photosensitive composition was washed away from its support layer with warm water. The resulting transparencies were laminated to glossy black filled polyvinyl chloride to give an enlarged silverless, continuous tone, black and white, photographic print. It is to be understood that the transparency to be enlarged by this process can be a halftone, continuous tone, or a line transparency.

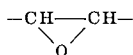
The following example shows a method of forming direct prints in a camera from a white-pigmented photosensitive composition.

EXAMPLE 49

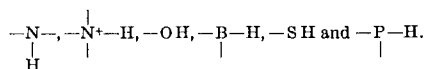
10 g. of Prepolymer S from Example 20, 2.72 g. of pentaerythritol tetrakis (β -mercaptopropionate), 3.0 g. titanium dioxide pigment and 3.0 g. dibenzosuberone were mixed together and heated in a vacuum oven for 5 minutes at 110° C. A 2 mil film of this material was spread on a sheet of cellulose acetate (5 mil thick) and a 5 mil thick sheet of cellulose acetate was rolled on top of the photosensitive material to produce a sandwich of the photographic film. The sandwich was put in a film holder and the holder was placed in a No. 4 Xerox camera containing a *f* 16 lens. The camera was focused on a continuous tone black and white print which was illuminated by four 1,000 watt lamps. The film was exposed to UV light reflected from the continuous tone print for a period of 5 minutes and then the film was turned over and reexposed on its other side for an additional period of 5 minutes. The film sandwich was removed from the film holder, stripped apart and developed by washing in water at 60° C. until the uncured portion of the photosensitive composition was removed from each support. The thus formed positive images were laminated to black pigmented glossy polyvinyl chloride background material to give positive, silverless, black and white, continuous tone, photographic prints.

In practicing the instant invention, it should be understood that all the various combinations of polyenes and polythiols disclosed herein are operable in all the various processes disclosed and claimed herein. Thus, in the photosensitive material used in all the various processes, operable polyenes include, but are not limited to, 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; styrene/butadiene rubber; 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; the reaction product of a polyester diol and allyl isocyanate in a mole ratio of 1:2 respectively; the reaction product of polyoxypropylene diol having a molecular weight in the range of about 700-4,000, tolylene 2,4-diisocyanate and allyl alcohol in a mole ratio of 1:2:2 respectively; 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; the reaction product of polyethylene ether glycol having a molecular weight in the of about 600 to 6,000 and allyl isocyanate in a mole ratio of 1:2 respectively; 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, poly-1,3-butadiene; the triacrylate of the reaction product of trimethylol propane and ethylene oxide; triallyl urea; cellulose acetate methacrylate; the reaction product of 1,4-butanediol and allyl isocyanate in a mole ratio of 1:2 respectively; the reaction product of poly (tetramethyleneether) glycol, tolylene diisocyanate and allyl alcohol in a mole ratio of 1:2:2 respectively; and the polyene formed by reacting either (a) an organic epoxide containing at least two



groups in its structure with a member of the group consisting of hydrazine, primary amines, secondary amines, tertiary amine salts, organic alcohols and organic acids wherein said group members contain at least one organic substituent containing a reactive ethylenically or ethynically unsaturated group, or, (b) an organic epoxide containing at least one organic substituent containing a reactive ethylenically or ethynically unsaturated group with a member of the group consisting of hydrazine and an organic material containing at least two active hydrogen functions from the group consisting of



Any of the various polythiols encompassed by the definition herein are operable with the aforesaid polyenes in any of the herein disclosed and claimed processes to form the cured polythioether products of the instant invention.

The composition used for forming the silverless photographic images of the instant invention comprises

1. a liquid photosensitive material having a viscosity in the range 0 to 20 million centipoises at 130° C., said material consisting essentially of (a) a polyene containing at least two reactive unsaturated carbon to carbon bonds per molecule and (b) 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 than 4,

2. 0.0005 to 33 percent by weight of said composition of a photosensitizer and

3. a member of the group consisting of 1 to 25% by weight of said composition of a pigment and 0.1 to 25% by weight of said composition of a dye, the weight ratio of the polyene to the polythiol being 2-98:98-2 respectively.

What is claimed is:

1. A process for forming two silverless continuous tone photographic images from a single layer of photosensitive material which comprises forming a photographic film by sandwiching a layer adjusted to a uniform thickness in the

range 2 to 50 mils of a composition consisting essentially of a uniform mixture of (1) a liquid photosensitive material having a viscosity in the range 0 to 20 million centipoises at 130° C. consisting essentially of 98 to 2 percent by weight of said composition of a polyene containing at least 2 reactive unsaturated carbon to carbon bonds per molecule and 2 to 98 percent by weight of said composition of a polythiol containing at least 2 thiol groups per molecule, the total combined functionality of (a) the reactive unsaturated carbon to carbon bonds per molecule in the polyene and (b) the thiol groups per molecule in the polythiol being greater than 4; (2) 0.0005 to 33 percent by weight of said composition of a photosensitizer and (3) a member of the group consisting of 1 to 25 percent by weight of said composition of a pigment and 0.1 to 25 percent by weight of a dye between two support films both of which are transparent to actinic radiation, exposing said composition on both its surfaces either simultaneously or concurrently to actinic radiation through an image-bearing, continuous tone, transparency maintained adjacent to said transparent support film, whereby portions of the composition exposed to actinic radiation on the transparent support film proximate the actinic radiation source solidify to form a reverse image relative to said image-bearing transparency, separating said image-bearing support films and removing soluble portions of the composition in the unexposed areas thereby forming a silverless, continuous tone, photographic image on each support film.

2. The process according to claim 1 wherein said resultant photographic image is laminated to a substantially non-transparent, contrasting background material to give a silverless continuous tone, photographic print.

3. The process according to claim 2 wherein the background material is white.

4. The process according to claim 1 wherein the support film is a member of the group consisting of plastic, glass, and quartz.

5. The process according to claim 4 wherein the plastic is a member of the group consisting of polyethylene, polypropylene, poly-4-methylpentene, polystyrene, polyethylene terephthalate and cellulose acetate.

6. The process according to claim 1 wherein the composition contains in addition a member of the group consisting of a plasticizer, a filler, an odor mask, a light scattering agent and an antioxidant in an amount equal to 0.0005 to 500 parts per 100 parts of the composition.

7. The process according to claim 1 wherein the photosensitizer is a member of the group consisting of benzophenone, acetophenone, acenaphthene-quinone, methyl ethyl ketone, valerophenone, hexanophenone, α -phenyl-butyrophenone, p-morpholinopropiophenone, dibenzosuberone, 4-morpholinobenzophenone, 4'-morpholinodeoxybenzoin, p-diacylbenzene, 4-aminobenzophenone, 4'-methoxyacetophenone, benzaldehyde, α -tetralone, 9-acetylphenanthrene, 2-acetylphenanthrene, 1-thioxanthene, 3-acetylphenanthrene, 3-acetylindole, 9-fluorenone, 1-indanone, 1,3,5-triacetylbenzene, thioxanthene-9-one, xanthrene-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.

8. A process for forming two silverless, continuous tone, photographic images from a single photosensitive layer in a camera which comprises forming a photographic film by sandwiching a layer adjusted to a uniform thickness in the range 0.2 to 50 mils of a composition consisting essentially of a uniform mixture of (1) a liquid photosensitive material having a viscosity in the range 0 to 20 million centipoises at 130° C. consisting essentially of 98 to 2 percent by weight of said composition of a polyene containing at least 2 reactive unsaturated carbon to carbon bonds per molecule and 2 to 98 percent by weight of said composition of a polythiol containing at least 2 thiol groups per molecule, the total combined functionality of

(a) the reactive unsaturated carbon to carbon bonds per molecule in the polyene and (b) the thiol groups per molecule in the polythiol being greater than 4; (2) 0.0005 to 35 percent by weight of said composition of a photosensitizer and (3) a member of the group consisting of 1 to 25 percent by weight of said composition of a pigment and 0.1 to 25 percent by weight of a dye, between two support films both of which are transparent to actinic radiation, inserting the thus formed photographic film in a camera, exposing said photographic film to actinic radiation reflected from a continuous tone scene onto said composition thereby causing portions of the composition exposed to actinic radiation to form a solidified reverse image relative to said scene on transparent support film proximate the aperture and/or lens system, turning the photographic film over and exposing the other side of said composition to actinic radiation reflected from a continuous tone scene onto said composition thereby causing portions of the composition exposed to actinic radiation to form a solidified reverse image relative to said scene on said other transparent support film, removing said photographic film sandwich from said camera, separating said support films and removing the soluble unexposed portion of the photosensitive composition from both support films thus forming a silverless, continuous tone, photographic image on each support film.

9. The process according to claim 8 wherein the resultant image is laminated to a substantially non-transparent, contrasting background material to give a continuous tone photographic print.

10. A process for forming two silverless half tone photographic images from a single photosensitive layer in a camera which comprises forming a photographic film by sandwiching a layer adjusted to a uniform thickness in the range 0.2 to 50 mils of a composition consisting essentially of a uniform mixture of (1) a liquid photosensitive material having a viscosity in the range 0 to 20 million centipoises at 130° C. consisting essentially of 98 to 2 percent by weight of said composition of a polyene containing at least 2 reactive unsaturated carbon to carbon bonds per molecule and 2 to 98 percent by weight of said composition of a polythiol containing at least 2 thiol groups per molecule, the total combined functionality of (a) the reactive unsaturated carbon to carbon bonds per molecule in the polyene and (b) the thiol groups per molecule in the polythiol being greater than 4; (2) 0.0005 to 33% by weight of said composition of a photosensitizer and (3) a member of the group consisting of 1 to 25 percent by weight of said composition of a pigment and 0.1 to 25 percent by weight of a dye, between two support films both of which support films are transparent to actinic radiation, inserting the thus formed photographic film in a camera, exposing said photographic film through a screen to actinic radiation reflected from a continuous tone scene onto said composition thereby causing portions of the composition exposed to actinic radiation to form a solidified reverse image relative to said scene on said trans-

parent support film proximate the aperture and/or lens system, turning the photographic film over and exposing the other side of said composition through a screen to actinic radiation reflected from a continuous tone scene onto said composition thereby causing portions of the composition exposed to actinic radiation to form a solidified reverse image relative to said scene on said other transparent support film, removing said photographic film sandwich from said camera, separating said support films and removing the soluble unexposed portion of the photosensitive composition from both support films thus forming a silverless, half tone, photographic image on each support film.

11. The process according to claim 10 wherein the halftone image is used directly or is laminated to a transparent background material to give a half tone transparency.

12. The process according to claim 10 wherein the half tone image is laminated to a substantially non-transparent, contrasting, background material to give a half tone photographic print.

13. A process for forming two enlarged, silverless, continuous tone, photographic images from a single layer of photosensitive material which comprises forming a photographic film by sandwiching a layer adjusted to a uniform thickness in the range 2 to 50 mils of a composition consisting essentially of a uniform mixture of (1) a liquid photosensitive material having a viscosity in the range 0 to 20 million centipoises at 130° C. consisting essentially of 98 to 2 percent by weight of said composition of a polyene containing at least 2 reactive unsaturated carbon to carbon bonds per molecule and 2 to 98 percent by weight of said composition of a polythiol containing at least 2 thiol groups per molecule, the total combined functionality of (a) the reactive unsaturated carbon to carbon bonds per molecule in the polyene and (b) the thiol groups per molecule in the polythiol being greater than 4; (2) 0.0005 to 33 percent by weight of said composition of a photosensitizer and (3) a member of the group consisting of 1 to 25 percent by weight of said composition of a pigment and 0.1 to 25 percent by weight of said composition of a dye between two support films both support films being transparent to actinic radiation, projecting the actinic radiation in an enlarger apparatus through an image-bearing transparency mounted in the slide-holder provided, through the lens system onto one surface of said composition for a time sufficient to solidify the portions of said composition exposed to actinic radiation, in like matter exposing the other surface of said composition separating said support films and removing the soluble unexposed portion of the photosensitive composition from both support films thus forming an enlarge, silverless, continuous tone, photographic image on each support film.

14. The process according to claim 13 wherein the resultant enlarged image is laminated to a substantially non-transparent, contrasting background material to give a continuous tone photographic print.

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