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SILVERLESS PHOTOGRAPHIC PRINTING PAPER

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ABSTRACT OF THE DISCLOSURE

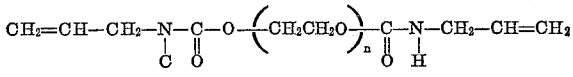
This invention relates to a novel polyethylene glycol-containing polyene which in combination with a polythiol, photosensitizer and pigment adhered to at least one UV transparent film by an adhesive layer can be used as a silverless photographic printing paper which can be developed by washing in warm water.

This invention relates to silverless photography and to a silverless photographic printing paper which can be developed in water.

Continuous tone photographic materials used today consist of silver halid emulsions coated on supports, the silver halide being converted to metallic silver by the action of light and developer. The system has several disadvantages. One disadvantage is the high cost of silver due to silver being in such short supply. Another drawback is that all development work must be done in the dark, thus necessitating costly darkrooms. Still another drawback is that the development requires the use of costly developing chemicals, such as developer, shortstop and fixer.

One object of the present invention is to produce a novel water soluble polyene. Another object of the invention is to produce compositions of said polyene in combination with a polythiol, photosensitizer and a pigment or dye which are photocurable. Still another object is to produce photocurable compositions which are useful in the photographic industry. A further object of the instant 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 photographic films and prints which can be developed in water.

Summarily the novel water soluble polyene of this invention is formed by reacting a polyethyleneether glycol having a molecular weight in the range 200–6000 with allyl isocyanate in a 1:2 mole ratio respectfully. Polyethyleneether glycols of varying molecular weights can be reacted together with the allyl isocyanate. The reaction may if desired be carried out in the presence of a catalyst. Tin catalysts such as dibutyl tin dilaurate, stannous octoate and tertiary amines such as triethylene diamine are operable in porducing the polyene of the instant invention. The reaction is usually performed at a temperature in the range 20–100° C., preferably 60–75° C. The water soluble polyenes useful for photographic work have molecular weights in the range 375–6000. Higher molecular weight polyenes because of their viscosity do not wash out readily in the development step when they are used to make photographic transparencies and prints. The novel water soluble polyene of this invention has the general formula:



wherein n is 2 to 135.

Additionally, silverless photographic images and prints which can be developed in water under normal lighting conditions can be prepared from a layer adjusted to a uniform thickness in the range 0.1–50 mils of photosensitive composition having a viscosity in the range 0–20 million centipoises at 130° C., said photosensitive composition comprising a photosensitizer, a polythiol, a pigment or a dye and the polyene of this invention, 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, said layer being supported on and adhered to at least one UV transparent film by a process comprising exposing said composition through its support film to actinic radiation through an image-bearing transparency, thereby causing the exposed portions of the composition to form a solidified image on said support layer and removing the unsolidified portions of the composition to form an image by developing the composition in water.

Said image, if positive, can be laminated to a contrasting background mateiral, e.g., a high reflectance material to give a continuous tone photographic print. The layer of the photosensitive composition may be, if desired, sandwiched between two films at least one of which transmits actinic radiation. The sandwich is peeled apart after exposure and the composition on the UV transparent film proximate the actinic radiation solidifies to form a latent image which can be developed in warm water. Depending upon whether the dye or pigment in the photosensitive composition is black or white, the resultant image will form a photographic print on being laminated to the opposite colored background material.

The UV transparent 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 and which can transmit a substantial amount of UV light. Operable plastics include, but are not limited to, polyethylene, polypropylene, poly-4-methylpentene, polystyrene, polyethylene terephthalate, i.e., "Mylar," cellulose acetate and the like. The thickness of the support is dependent upon 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 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-retardant agents, thickeners, thixotropic 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 polyene or polythiol prior to or during the compounding step. 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 composition. The aforesaid additives may be present in quantities up to 500 parts of more per hundred parts of the 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 photo curing image-producing reaction or other required steps in the photographic process.

Additionally, 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 photosensi-

tized image is laminated to a piece of high reflecting 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 themal blacks having particle diameters of 5–250 millimicrons. Black dyes which are generally azine and azo organic compounds are also operable. The white pigments including TiO_2 are also operable.

For colored prints any suitable colored dye is operable that does not contain groups which would inhibit the curing system employed.

In practicing the instant invention, the photosensitive composition is usually adhered to the UV transparent support layer by means of an adhesive layer. Conventional adhesives are operable although preferably a photocurable adhesive such as disclosed in U.S. 617,801, filed Feb. 23, 1967 and assigned to the same assignee are preferred. The adhesive layer is usually applied as a solution in alcohol as a thin layer onto the UV transparent support. The alcohol is then evaporated and the remaining photocurable liquid polymer is cured by direct exposure to UV light. Thereafter, the photosensitive composition of the instant invention is applied to the adhesive layer and is ready for use. If desired, a second adhesive layer with another support layer can be added to the top of the photosensitive composition of the instant invention to produce a sandwich. The thickness of the adhesive layer is dependent upon the thickness of the photosensitive composition which will be applied thereon, with a greater thickness required in the adhesive layer for a greater thickness of the photosensitive composition. Ordinarily, the adhesive layer will have a thickness in the range 0.01–5 mils, however, thicknesses greater than 5 mils may be employed if necessary. The adhesive layer is a clear photocurable composition which solidifies on exposure to actinic radiation.

In the instant invention the photosensitive composition consists of 2 to 98 parts by weight of the polyethyleneether glycol-containing polyene which contains at least 2 reactive unsaturated carbon to carbon bonds per molecule, 98 to 2 parts by weight of a polythiol containing 2 or more 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, a photosensitizer in an amount ranging from 0.0005 to 50% by weight, suitably 0.0005 to 25% by weight and when used for photographic purposes a member of the group consisting of 1–25% by weight of a pigment and 0.1–25% by weight of a dye.

As used herein, the term "polythiol" refers to the simple or complex organic compounds having a multiplicity, i.e., at least 2, of pendent 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 0–20 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 have molecular weights in the range 50–20,000, preferably 100–10,000.

The polythiols ooerable 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 unsaturation.

One class of polythiols operable with the polyene of the instant invention to obtain a cured polythioether photographic medium is 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: $R_{10}(OH)_n$ 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:

$$R_{10}—\left(\begin{matrix}O\\ \|\\ C—R_9—SH\end{matrix}\right)_n$$

wherein 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(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.

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.

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. 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 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 swellable, chain-extended composition which is unsuitable for the purpose of this invention. Thus, in practicing the instant invention to obtain a solid photocured 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 (a) the unsaturated carbon to carbon bonds per molecule of polyene and (b) the thiol groups per molecule of polythiol is greater than four.

The curing reaction to form cured polythioether can be initiated by any free radical mechanism which dissociates or abstracts a hydrogen atom from the SH group (or accomplishes the equivalent thereof) and which is operable under ambient conditions. Thus, it is possible merely to expose the polyene and polythiol admixture to ambient conditions (oxygen from the air is the initiator) and obtain a cured solid elastomeric or resinous polythioether product. Azo compounds or peroxides (with or without amine accelerators) which decompose at ambient conditions are also operable as free radical generating agents capable of curing the components of the instant invention to solid elastomeric or resinous polythioether products. Additionally, ultraviolet light or other forms of energetic radiation yield rapid cures by the practice of the instant invention.

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 photosensitive composition through the transparent support film and a positive transparency to actinic radiation preferably in the range 2200–4000 A. under ambient conditions or otherwise and obtain a solid latent image-containing product useful as a photographic material after development in water.

The photosensitive reaction rate is increased by the use of a photosensitizer.

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, 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, suitably 0.0005 to 33% by weight, preferably 0.5 to 25% of the photosensitive composition of 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. Hence photographic printing materials 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, the liquid photocurable composition consisting of the polyene, the polythiol and any other additives, e.g., photosensitizer pigment or dye, may be 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, 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.) 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 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. 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 UV 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 UV through the support from underneath the support.

The development of the exposed film is carried out by immersing it in water, preferably warm water, i.e., 35–50° C. The development may require periods ranging from 5 seconds up to 20 minutes or more depending on the thickness of the layer of the photosensitive composition. The development can be aided by mechanical means such as blotting with a sponge. Such development releases the uncured photosensitive composition from the support layer.

A convienent 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 dyed filled photosensitive composition which has been adhered by an adhesive layer to a transparent support and adjusted for uniformity by suitable means, e.g., a drawbar, precast mold or the like. The layer of the photosensitive composition can be covered with an additional adhesive layer adhering to a film layer to form a sandwich, if desired. The layer of the photosensitive composition is exposed through the transparency and its transparent support to a source of actinic light suitably in the wave length range 2200–4000 A. until the layer is cured 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 peeled apart leaving on the transparent support, a latent cured solidified reverse image and uncured polymer. The transparent support bearing said image is then subjected to development by removal of the uncured polymer in a warm water bath. 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 after development to UV radiation for periods up to 10 minutes to further harden it.

The resultant 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 an conventional process.

(2) If the transparency is a positive it may be laminated with an adhesive to a contrasting black or white reflecting background material to give a black and white print. 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 and the photosensitive composition by use of suitable dyes or pigments. Preferred backings are paper, vinyl and any other pigmented plastics.

(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 explaining, 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

Preparation of the polyene

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 4000 (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 Polymer A.

EXAMPLE 2

Preparation of the adhesive coated support layer

To a 2-liter flask equipped with stirrer, thermometer and gas inlet and outlet was charged 450 grams (0.45 moles) of a polytetramethyleneether glycol having a hydroxyl number of 112 and a molecular weight of approximately 1000 along with 900 grams (0.45 moles) of polytetramethyleneether 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 grams of dibutyl tin dilaurate was added to the flask. A mixture of 78 grams (0.45 moles) of tolylene diisocyanate and 77 grams (0.92 moles) of allyl isocyanate was then added to the flask dropwise with stirring. The reaction was maintained at 70° C. for 1 hour after addition of the reactants. The thus formed allyl-terminated polymer will hereinafter be referred to as Polymer X.

10 grams of Prepolymer X, 0.77 grams pentaerythritol tetrakis (β-mercaptopropionate) and 0.15 grams benzophenone were admixed in 100 ml. of isopropanol for 30 minutes to obtain a homogenous mixture of the adhesive layer. A ½ mil film of the adhesive layer was uniformly coated on a clear UV transparent polystyrene film (5 mils thick). The coating was then exposed directly to a 4000 watt Ascrolux pulsed xenon arc lamp for 1 minute to cure the adhesive layer on the polystyrene support film. This operation was repeated to form another adhesive layer on another polystyrene support film of the same dimensions and properties.

EXAMPLE 3

Preparation of photosensitive composition

20 grams of Polymer A, 6.6 grams of pentaerythritol tetrakis (β-mercaptopropionate), 2.0 grams of benzophenone, 2.0 grams of polymethyl vinyl ether and 0.75 grams carbon black (Sterling FT) were admixed together and stirring was continued for 30 minutes to obtain a uniform mixture. The thus formed photosensitive polymer composition was then coated by means of a drawbar onto the adhesive treated side of one of the polystyrene films from Example 2 and the other adhesive treated polystyrene film was rolled on top of the photosensitive composition to produce a sandwich. The thickness of the photosensitive composition was 2 mils.

EXAMPLE 4

Preparation of photographic image and print

The thus formed sandwich of Example 3 was exposed under and in contact with a photographic negative to a 4000 watt Ascrolux pulsed xenon arc lamp 19" away for 20 seconds. Upon peeling the sandwich apart, a positive continuous image i.e., reversed relative to the negative, of cured polythioether was formed on the clear polystyrene proximate the continuous tone negative through which the light passed. Uncured polymer was removed from the polystyrene layer by rinsing said layer in warm water at a temperature of 40–50° C. for 15 seconds. 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

appearance 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 5

The photosensitive polymer composition of Example 3 was admixed and used to form a sandwich between adhesive layers on polystyrene backing, except that the 0.75 grams carbon black (Sterling FT) was substituted by 1.0 gram of white TiO_2 pigment.

The thus formed sandwich was exposed through a continuous tone photographic positive transparency to a 4000 watt Ascrolux pulsed xenon arc printing lamp situated 19" away for 30 seconds. Upon peeling the sandwich apart the polystyrene support layer proximate the transparency had a cured latent image thereon. The image bearing polystyrene layer was subjected to a warm water wash at 50° C. for 15 seconds to remove the uncured polymer from the unexposed areas. The thus formed image was then dried and laminated to a piece of high reflectance black paper to give a silverless, black and white continuous tone photographic print. The visual appearance 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 silver halide technology.

EXAMPLE 6

The procedure and reactants of Example 5 were employed except that 2.00 grams of dibenzosuberone was substituted for the 2.0 grams of benzophenone and the exposure time was 5 seconds. The resulting black and white silverless print was of the same quality as in the previous example.

EXAMPLE 7

Example 4 was repeated except that "Mylar" was substituted for the clear polystyrene support layers. The resulting print was of the same quality.

EXAMPLE 8

Example 5 was repeated except that a polycarbonate film was used instead of the clear polystyrene support layer. The resulting print was of the same quality.

EXAMPLE 9

Example 4 was repeated except that Sterling FT carbon black was replaced by 1.0 gram of black dye, i.e., Aquaprint 0.5–5207 black K from Interchemical Co. The resulting print was of the same quality.

EXAMPLE 10

A sandwich of the photosensitive material of Example 3 was cut to 5 x 4" and the edges sealed by brief exposure to UV light. The "film" so obtained was loaded into Graphic cut film holders, and exposures were made in a Polaroid MP 4 Technical camera fitted with a Goerz Dagor lens. Illumination of the subject (a silver halide continuous tone black and white print) was supplied by two 275 watt sunlamps. Exposure time was 15 minutes at *f*4.5. The silverless photographic negative obtained, was developed by washing in warm water at 50° C. for 15 minutes. The negative was printed to give an excellent continuous tone silverless, black and white print using the procedure of Example 4. 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 4 except that carbon black was replaced by 3.5 grams of Adpro blue dye. The negative prepared through the green filter was printed using the procdure of Example 4 except that carbon black was replaced by 3.5 grams of Adpro yellow dye. The negative prepared through the blue filter was printed using the procedure of Example 4 except that carbon black was replaced by 3.5 grams 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 procedure of Example 11 was used except that the three colored images were then superimposed and laminated to a piece of clear "Mylar" to give a three color transparency.

The following example shows a method of varying the colors of a resultant print.

EXAMPLE 13

10 grams of Polymer A, 0.9 gram of pentaerythritol tetrakis (β-mercaptopropionate) and 1.5 grams phthalocyanine blue commercially available from Harshaw Chemical Co. in ethylene glycol monoethylether were admixed together and then heated in a vacuum oven for 5 minutes at 120° C. 0.2 gram of benzophenone was added to the mixture, and mixing was continued for 2 minutes. A 1-mil thick film of the photocurable mixture was spread on adhesive coated opaque "Mylar" and a sheet of clear "Mylar" was adhered 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 UV lamp situated 9" away for 3 minutes. The negative was removed and the sandwich was peeled apart, resulting in a latent positive image, i.e., one reverse to the photographic negative through which the light passed, was adhered to the clear "Mylar." The image was developed by removing uncured polymer from the clear "Mylar" by immersing it in a water bath at 50° C. for 20 seconds. The developed image 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 excelent quality and appearance.

EXAMPLE 14

Using conventional silver halide film, 3 separation negatives were prepared by photographing an outdoor scene with a 4 by 5 Calumet view camera (6½ inch Ilex-Calumet Caltar *f*6.3 lens) with the camera mounted on a tripod. The negatives were prepared through the following filters: Wratten No. 25 (red), Wratten No. 58 (green), Wratten No. 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 photosensitive composition of Example 3 except that 1.5 grams of Adpro blue dye was substituted for the 0.75 grams carbon black. The negative prepared through the green filter was printed using the composition of Example 3 except that 1.5 grams of Adpro yellow dye was substituted for the carbon black. The negative prepared through the blue filter was printed using the composition of Example 3 except that 1.5 grams of Adpro red dye was substituted for the carbon black.

For printing, each negative was placed over its aforestated photosensitive compositions of Example 3, sandwiched between pieces of clear polystyrene (each 5 mils thick and each having a layer of the adhesive of Example 2 of ½ mil thickness. The sandwich was exposed through the negative to a 275 watt UV lamp 9" away for 3 minutes for the photosensitive composition containing the blue dye, 4 minutes for the photosensitive com-

position containing the red dye and 1½ minutes for the photosensitive composition containing the yellow dye.

Each sandwich containing the photosensitized composition was then peeled apart and the latent image was developed by immersing the polystyrene layer with the latent image thereon in a warm water bath at 50° C. for 20 seconds to remove the uncured polymer. The images were then dried, laminated together in register and laminated to a white, opaque, high 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 15

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 3. The art work was illuminated by the 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 4, a silverless photographic negative was obtained. The overall time for the preparation of the negative (i.e., the combined exposure and development time was less than 6 minutes and no darkroom was required for this work.

The 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 copending application No. 674,773 filed Oct. 12, 1967 and assigned to the same assignee, (b) a photoengraving on metallic Zn using conventional photoresists and the powderless etching techniques (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 16

50 grams of Polymer A, 1.88 grams of carbon black (Sterling FT), 4.55 grams of pentaerythritol tetrakis (β-mercaptopropionate) were mixed together and heated in a vacuum over for 5 minutes at 120° C. 3.0 grams of dibenzosuberone were 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" coated with a ½ mil thick adhesive layer prepared as in Example 2 and a 1.0 mil thick sheet of clear "Mylar" coated with a ½ mil thick adhesive layer from Example 2 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 and a *f*4.5 135 mm. Kodak enlarging Ektanon lens and 275 watt UV lamp. A 35 mm. continuous tone negative was placed in the enlarger and the photocurable material was exposed through the negative to the UV 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 a warm water bath at 50° C. for 10 seconds to remove the uncured polymer. The developed positive image was dried and laminated to a white pigmentsd polyvinyl chloride sheet with a commercial spray adhesive "Quikstick" to give a silverless, enlarged, black and white, continuous tome, photographic print.

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

EXAMPLE 17

50 grams of Polymer A, 1.88 grams of carbon black (Sterling FT), 4.95 grams of trimethylol propane tris(β-mercaptopropionate) were mixed together and heated in a vacuum oven for 5 minutes at oven temperature of 20° C. 3 grams of dibenzosuberone were then added and mixing was continued for 2 minutes. A 1-mil layer of this photocurable material was spread on a sheet of clear "Mylar" (5.0 mils thick) containing a ½ mil layer of the adhesive of Example 2 thereon and another 5.0 mil thick sheet of clear "Mylar" also coated with the cured adhesive layer of Example 2 was rolled on top of the photocurable 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 UV 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 latent 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 latent image-containing sheet was developed by immersing it in a warm water bath at 60° C. for 15 seconds to remove uncured polymer. The positive image was dried and laminated to a sheet of white pigmented polyvinyl chloride with "Quickstick" a commercially available spray adhesive to give a silverless, black and white, continuous tone photographic print of excellent quality. The negative image-containing sheet was then reexposed directly to a 275 watt UV lamp for 1 minute to further harden the image. The thus reexposed negative image was laminated to a clear (5 mil thick) "Mylar" film with "Quikstick" 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.

EXAMPLE 18

Example 15 was repeated except that a halftone print was photographed to give a halftone negative.

The following example shows the method of using the instant invention to make an enlarged black and white print.

EXAMPLE 19

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 the photosensitive composition of Example 3 so that the image was 8 x 10" in size. The projector was equipped with a 500 watt DEK 120 volt, 60 cycle lamp which yielded an intensity of 380 microwatts/cm.^{2} at the enlarged area. After an exposure of 10 minutes, the sandwich was peeled apart and the positive image on the clear polystyrene was developed in a water bath at 60° C. for 10 seconds. The resulting transparency was laminated to a white pigmented polyvinyl chloride background to give a black and white print. It is to be understood that the negative to be enlarged by this process can be a halftone, continuous tone or a line negative. Additionally, colored negatives or transparencies can be enlarged into black and white prints by the practice of this example with longer exposure times.

The following example shows a method for using the instant invention in making a direct positive print from a negative.

EXAMPLE 20

30 grams of Polymer A, 2.72 grams of pentaerythritol tetrakis(β-mercaptopropionate), 3.0 grams TiO_2 pigment and 3.0 grams of dibenzosuberone were mixed together and then heated in a vacuum oven for 2 minutes at 120°

C. A 1-mil film of this material was spread on a sheet of UV transparent polystyrene (5 mil thick) having a layer of ½ mil of the adhesive composition of Example 2 thereon and a 5 mil thick sheet of UV transparent polystyrene also containing ½ mil layer of the adhesive of Example 2 was rolled on top of the photocurable material to produce a sandwich. The sandwich was exposed under a continuous photographic negative to a 4000 watt pulsed xenon arc lamp 19" away for 5 seconds. The sandwich was then peeled apart resulting in a latent negative image adhering to the upolystyrene layer proximate the negative, i.e., one identical to the photographic negative through which the light passed, and a direct image adhered to the polystyrene layer away from the negative, i.e., one reversed relative to the photographic negative through which the light passed. Uncured polymer was removed from the negative image by immersing it in a water bath at 60° C. for 10 seconds. The thus formed negative can now be used repetitively to produce positives by the contact method as shown herein in Example 4 and employing a black pigment or dye in the photosensitive composition. The bottom layer containing the positive image is then reexposed directly to a 4000 watt pulsed xenon arc lamp 19" away for an additional 5 seconds to cure the photosensitive composition remaining on the bottom polystyrene film layer. The thus cured positive image is then laminated to a piece of glossy black paper to give a silverless, continuous tone, black and white, photographic print.

EXAMPLE 21

Example 20 was repeated except that a positive transparency was used instead of a negative. The resultant image on the polystyrene proximate the positive transparency after washing in warm water at 60° C. was laminated to a glossy black background paper to give a direct positive print and the image formed on the bottom polystyrene film was reexposed to UV light for 5 seconds resulting in a negative image which can be used repetitively to form a positive by contact printing employing a white pigmented photosensitive composition.

EXAMPLE 22

10 grams of Polymer A, 0.9 grams of pentaerythritol tetrakis(β-mercaptopropionate), 1.0 grams of TiO_2 pigment were mixed together and then heated in a vacuum oven for 5 minutes at 120° C. 1.08 grams of dibenzosuberone was then added and mixing was continued for 2 minutes. A 1 mil film of this material was spread on a 5 mil thick sheet of UV transparent polystyrene having an adhesive layer ½ mil thick from Example 2 thereon and another 5 mil thick sheet of UV transparent polystyrene also containing a ½ mil adhesive layer from Example 2 was rolled on top of the photocurable material to produce a sandwich. The sandwich was exposed under a positive color transparency to a 4000 watt xenon arc lamp 19" away for 30 seconds. The sandwich was peeled apart resulting in a positive image identical to the positive color transparency through which the light passed adhering to the clear polystyrene proximate the positive transparency. Uncured polymer was removed from the positive image by immersing it in a water bath maintained at a temperature of 60° C. for 15 seconds. The positive image was removed, rinsed with water, dried, and laminated to a black pigmented polyvinyl chloride sheet with "Quikstick" to give a silverless, black and white, continuous tone, photographic print.

EXAMPLE 23

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 22 so that the image was 8 x 10 in size. The projector was equipped with a 500 watt DEK 120 volt 60 cycle lamp which yielded an intensity of 380 microwatts/cm.^{2} at the enlarged area. After an exposure of 10 minutes, the sandwich was peeled apart and the positive image on the polystyrene layer proximate the positive color transparency was developed by immersing it in a water bath at 50° C. for 10 seconds. The resulting transparency was laminated to a glossy, carbon black-filled polyvinyl chloride to give a black and white, continuous tone 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.

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

Examples 20–23 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 Examples 20–23) is accomplished by using a white pigmented photocurable composition as the image-forming photosensitive medium.

The net 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. However, one can obtain a positive print from a white-on-clear negative by printing this negative on the white-pigmented photocurable composition printing paper as described in the Examples 20–23. Conversely, one can obtain positive photographic prints by printing white-on-clear positives on conventional silver halide printing paper or on the black-pigmented photocurable composition printing paper of this invention.

Other unusual features of this new approach to photographic image formation will be obvious from inspection of Examples 20–23.

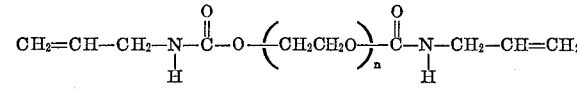
EXAMPLE 24

10 grams of Polymer A, 1.0 gram of pentaerythritol tetrakis(β-mercaptopropionate) and 3.0 grams of dibenzosuberone were admixed by hand in an aluminum weighing dish and exposed to a 4,000 watt pulsed xenon arc lamp for two minutes. A solid cured polythioether resulted.

I claim:

1. A silverless continuous tone photographic image consisting essentially of a pigment or dye filled cured polythioether in the image area formed from a photosensitive composition consisting essentially of

(a) 98–2 percent by weight of said composition of a water soluble polyene of the formula:



wherein n is 2 to 135,

(b) 2–98 percent by weight of said composition of a polythiol and mixtures thereof having a molecular weight in the range of 50–20,000 of the general formula: $R_8(SH)_n$ wherein R_8 is a polyvalent organic moiety free from reactive carbon to carbon unsaturation and n is at least 2, 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,

(c) 0.0005 to 33 percent by weight of said composition of a photosensitizer and

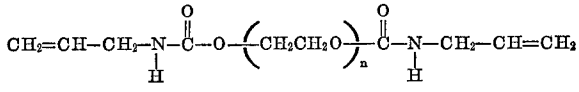
(d) a member of the group consisting of 1–25 percent by weight of said composition of a pigment and 0.1 to 25 percent by weight of said composition of a dye, said composition adhered to a transparent member of the group consisting of plastic and glass.

2. A silverless continuous tone photographic print consisting essentially of the silverless continuous tone photographic image adhered to the transparent group member of claim 1 laminated to an opaque background material.

3. The print according to claim 2 wherein the opaque background material is a member of the group consisting of plastic, paper, wood, metal, cloth, brick, motar, and glass.

4. A process for forming a silverless, continuous tone photographic image which comprises supporting a layer adjusted to a uniform thickness in the range of 0.1 to 50 mils of a photosensitive composition consisting essentially of

(a) 98–2 percent by weight of said composition of a water soluble polyene of the formula:



wherein n is 2 to 135,

(b) 2–98 percent by weight of said composition of a polythiol and mixtures thereof having a molecular weight in the range of 50–20,000 of the general formula: $R_8(SH)_n$ wherein R_8 is a polyvalent organic moiety free from reactive carbon to carbon unsaturation and n is at least 2, 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,

(c) 0.0005 to 33 percent by weight of said composition of a photosensitizer and

(d) a member of the group consisting of 1–25 percent by weight of said composition of a pigment and 0.1 to 25 percent by weight of said composition of a dye on a support film which is transparent to actinic radiation, exposing said composition to actinic radiation through the support film and through an image-bearing, continuous tone transparency maintained in contact with the support film and substantially parallel to the layer of said composition, thereby causing portions of the composition exposed to actinic radiation through the support film to form a cured solidified reverse image relative to said transparency and removing uncured portions of the composition in a water bath to form a continuous tone image.

5. The process according to claim 4 wherein the continuous tone image formed on the transparent support is laminated to a substantially non-transparent background material to give a continuous tone photographic print.

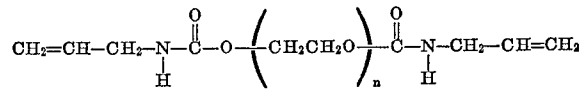
6. The process according to claim 5 wherein the background material is white.

7. The process according to claim 5 wherein the background material is black.

8. The process according to claim 4 wherein the continuous tone image formed on the transparent support film is laminated to a transparent background material to give a continuous tone photographic transparency.

9. A process for forming silverless continuous tone photographic images which comprises sandwiching a layer adjusted to a uniform thickness in the range 0.1 to 50 mils of a photosensitive composition consisting essentially of

(a) 98–2 percent by weight of said composition of a water soluble polyene of the formula:



wherein n is 2 to 135

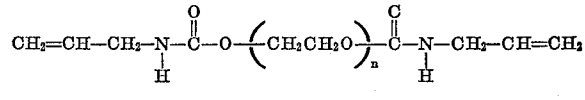
(b) 2–98 percent by weight of said composition of a polythiol and mixtures thereof having a molecular weight in the range of 50–20,000 of the general formula: $R_8(SH)_n$ wherein R_8 is a polyvalent organic moiety free from reactive carbon to carbon unsaturation and n is at least 2, the total combined functionality of the reactive unsaturated carbon to carbon bonds per molecule in the polyene and thiol groups per molecule in the polythiol being greater than 4,

(c) 0.0005 to 33 percent by weight of said composition of a photosensitizer and

(d) a member of the group consisting of 1–25 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, at least one of which is transparent to actinic radiation, exposing said composition to actinic radiation through an image-bearing continuous tone transparency maintained in contact with the transparent support film 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 solidifies to form a reverse image relative to said transparency and adhere to said transparent support film, separating said image-bearing support film from the other support film, said other support film having adhered thereto substantially all of the unexposed composition, developing the image-bearing support film in a water bath and forming a direct image on the other support film by re-exposing the composition thereon directly to actinic radiation, thus forming two continuous tone images, one being a positive and the other a negative.

10. A color process which comprises exposing individually to UV radiation three separation negatives prepared through red, green and blue filters respectfully while maintaining said negative adjacent to and in contact with a UV transparent film supporting a layer adjusted to a uniform thickness in the range of 0.1 to 50 mils of a photosensitive composition consisting essentially of

(a) 98–2 percent by weight of said composition of a water soluble polyene of the formula:



wherein n is 2 to 135,

(b) 2–98 percent by weight of said composition of a polythiol and mixtures thereof having a molecular weight in the range of 50–20,000 of the general formula: $R_8(SH)_n$ wherein R_8 is a polyvalent organic moiety free from reactive carbon to carbon unsaturation and n is at least 2, the total combined functionality of the reactive unsaturated carbon to carbon bonds per molecule in the polyene and thiol groups per molecule in the polythiol being greater than 4,

(c) 0.0005 to 33 percent by weight of said composition of a photosensitizer and

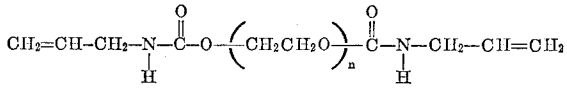
(d) a member of the group consisting of 1–25 percent by weight of said composition of a pigment and 0.1 to 25 percent by weight of said composition of a dye, said composition adjacent the separation negative prepared through the red filter containing a cyan pigment or dye, said composition adjacent the separation negative prepared through the green filter containing a magenta pigment or dye and said com-

position adjacent the separation negative prepared through the blue filter containing a yellow pigment or dye, developing the supported cyan, magenta and yellow positive image transparency individually by removing uncured portions of the composition from the respective layers in a water bath and laminating the cyan, magenta and yellow transparencies in register to obtain a full color continuous tone transparency.

11. The process according to claim **10** wherein the full color transparency is laminated to a substantially non-transparent background material to obtain a full color print.

12. A process for forming silverless continuous tone photographic images which comprises sandwiching a layer adjusted to a uniform thickness in the range 0.1 to 50 mils of a photosensitive composition consisting essentially of

(a) 98–2 percent by weight of said composition of a water soluble polyene of the formula:



wherein n is 2 to 135,

(b) 2–98 percent by weight of said composition of a polythiol and mixtures thereof having a molecular weight in the range of 50–20,000 of the general formula: $R_8(SH)_n$ wherein R_8 is a polyvalent organic moiety from reactive carbon to carbon unsaturation and n is at least 2, 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,

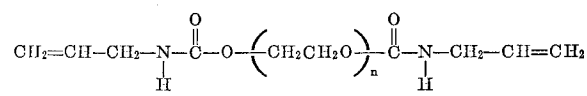
(c) 0.0005 to 33 percent by weight of said composition of a photosensitizer and

(d) a member of the group consisting of 1–25 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, at least one of which is transparent to actinic radiation, exposing said composition to actinic radiation through an image-bearing continuous tone transparency maintained in contact with the transparent support film 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, solidify to form a reverse image relative to said transparency and adhere to said transparent support film, separating said image-bearing support film from the other support film and thereafter developing the image-bearing support film in a water bath to form a continuous tone image.

13. A process for forming an enlarged, silverless, black and white continuous tone photographic transparency which comprises

(1) projecting the actinic radiation in a slide projector or enlarger through an image-bearing transparency mounted therein in the slide holder provided through the lens system onto a photosensitive composition sandwiched between two support films at least one of which is UV transparent and adherent to said composition, said composition having a uniform thickness in the range 0.1 to 50 mils and consisting essentially of

(a) 98–2 percent by weight of said composition of a water soluble polyene of the formula:



wherein n is 2 to 135,

(b) 2–98 percent by weight of said composition of a polythiol and mixtures thereof having a molecular weight in the range of 50–20,000 of the general formula: $R_8(SH)_n$ wherein R_8 is a polyvalent organic moiety free from reactive carbon to carbon unsaturation and n is at least 2, 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,

(c) 0.0005 to 33 percent by weight of said composition of a photosensitizer and

(d) a member of the group consisting of 1–25 percent by weight of said composition of a pigment and 0.1 to 25 percent by weight of said composition of a dye for a time sufficient to solidify the portions of said composition exposed to actinic radiation, thus forming on the transparent support film proximate the mounted transparency an enlarged image bearing transparency separating said image-bearing support film from the other support film and

(2) removing the uncured portion of the composition from the image-bearing support film in a water bath thus forming an enlarged reverse image transparency.

14. The process according to claim **13** wherein the image-bearing transparency to be enlarged is a color transparency.

15. The process according to claim **13** wherein the image-bearing transparency to be enlarged is black and white.

16. The process according to claim **13** wherein said resultant enlarged transparency is thereafter laminated to a substantially non-transparent background material to give a photographic print.

17. The process according to claim **16** wherein the background material is white.

18. The process according to claim **13** wherein the enlarged transparency is laminated to a transparent background material to give a photographic transparency.

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U.S. Cl. X.R.

96—27, 28, 115; 95—1